DEPARTMENT OF MECHANICAL ENGINEERING

FINAL REPORT ON THE EVALUATION OF
AL-LI-X TERNARY PHASE DIAGRAMS

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Evaluation of Al-Li-X Ternary Phase Diagrams

Contract Serial Number OST85-00041

Department of Energy, Mines and Resources

Executive Summary

A comprehensive literature survey was conducted to obtain relevant data on Al-Li-X Ternary alloys. Sufficient data were found to construct at least partial (Al-rich) ternary phase diagrams for five systems, Al-Li-Mg, Al-Li-Mn, Al-Li-Si, Al-Li-Zn and Al-Cu-Li. A critical evaluation of the literature of each of these systems is included in Parts I to V of this report respectively.

Part V (Al-Cu-Li System), which has been critically evaluated by Professor D.P. Miodownik and V.G. Rivlin in the United Kingdom, however, is requested to be kept confidential until it has been published in U.K. A bibliography for Al-Li-X ternary systems investigated but for which there is insufficient data to construct even a partial ternary diagram is included in Part VI and Appendix B.

Results of our experimental work to clear the confusion concerning the Phases in the composition range 35 wt.% - 50 wt.% Mg of the Al-Mg binary system are presented and discussed in Part VII. The experimental technique of utilizing liquid diffusion couples for the rapid determination of Phase diagrams, as applied to the Al-Mg system is also described in Part VII. The modifications in the liquidus projection of the Al-Li-Mg system arising as a result of this investigation are included in Appendix A.

Evaluation des diagrammes de phase ternaires Al-Li-X

Numero de Serie du Contrat OST85-00041

Department d'energie, mines et ressources

Sommaire:

Nous avons fait une etude intensive de la litterature pour obtenir des données sur les alliages Al-Li-X. On a trouvé assez de données pour construire partiellement un diagramme de phase (enrichi en Al) pour les systemes Al-Li-Mg, Al-Li-Mn, Al-Li-Si, Al-Li-Zn et Al-Cu-Li. Les sections I a V de ce rapport contiennent une evaluation critique de la litterature sur ces systemes respectivement.

La Partie V (Systeme Al-Cu-Li), qui a été évalué par le professeur D.P. Miodownik et V.G. Rivlin en Grande Bretagne doit été gardée confidentiellement jusqu'a sa publication en Grande Bretagne. La section Vi et l'Annexe B contient une bibliographie des systemes Al-Li-X où les données ne sont pas suffisantes pour construire un diagramme de phase.

Les resultats de nos travaux experimentaux pour clarifier la confusion a propos des phases dans les limites de composition entre 35% - 50% (poids) Mg dans le systems binaire Al-Mg sont présentés et discutés dans la Partie VII. Aussi dans la Partie VII, on decrit la technique experimentale de l'utilisation de diffusion de couples dans l'état liquide pour l'evaluation rapide des diagramme de phases du systéme Al-Mg. Les modifications dans la projéction du liquidus du systéme Al-Li-Mg qui ont été déterminés lors de cette étude sont inclus dans l'Annexe A.

ACKNOWLEDGEMENTS

This comprehensive report on the evaluation of Al-Li-X ternary phase diagrams is an outcome of the extensive efforts of Dr. Naresh C. Goel. Thanks are due to Mr. Don Himbeault who did some of the initial work for Part I of this report and to Mr. H. Weiss, Professor Hawaleshka and Dr. A. DeGroot who helped with the Russian and German translations needed in the preparation of Part I. Thanks are also due to Mr. B. Mikkelson who did part of the experimental work for Part VII of this report. Last but not least thanks are due to Gayle Ferguson and Kris Nabess for carefully typing this report.

Aluminum-Lithium-X Ternary Systems

Part I

The Al-Li-Mg (Aluminum-Lithium-Magnesium) System

26.98154 6.941 24.305

INTRODUCTION

Investigations of the Al-Li-Mg ternary system began with [48SHA] who provided a complete description of the liquidus projection and an isotherm at 400°C. Two later investigations of the liquid-solid equilibria are due to [77DRI] and [81SCH]. Isothermal sections at 375, 200 and 100°C by [55ROW], at 400, 300, 200 and 100°C by [55LEV, 56LEV], at 430 and 200°C by [73DRI] and at 300°C by [76PAD] have also been experimentally investigated. [77SAB] have theoretically calculated the isothermal section at 500, 450, 400 and 375°C from thermodynamic considerations. In the course of a comprehensive study of the Al-Li-Mg ternary system and of the associated binaries using modern analytical techniques, [80SCH & 81SCH] have studied some 178 alloys providing a complete description of the liquid-solid equilibria as well as isothermal sections at 400, 300 and 200°C. Solid solubility data are available from the work of [65FRI] as also from [73DRI] and [80SCH]. Some of these studies are corroborative while others are contradictory in providing the phase relationships in the Al-Li-Mg ternary system. The main reasons for disagreement have, however, been due to the uncertainty of the corresponding binary phase diagrams and due to the contradictory evidence concerning the occurrence of ternary compounds.

Despite the minor controversies still existing regarding the phase relationships in the Al-Li and Al-Mg binaries, the constituent binary phase diagrams are sufficiently well established [82McA, 84NAY, 82MUR, 80SCH] to permit a critical evaluation of the Al-Li-Mg ternary system.

The latest information on these binaries has been incorporated in the present assessment of the ternary system.

Recent works of [80SCH] and [81SCH] are considered to reasonably represent the phase relationships in the Al-Li-Mg ternary system. Some uncertainty still exists in the region 50-65% Al and 15-0 % Li. The phase relationships in the Li rich corner of the system are also in doubt with thermodynamic calculations of [77SAB] making curious predictions. However, experimental verification is difficult to obtain because of the extreme reactivity of the alloys at Li-corner.

Some features of this evaluation are speculative because of lack of availability of acceptable experimental data. These speculative features, however, are based on the evaluated data or are inferred from them and are clearly indicated as such. In order to avoid confusion concerning the use of different designations for the phase fields by various authors, the formulae for corresponding binary phases in addition to their symbols have been used even when referring to phase fields in the ternary system.

BINARY SYSTEMS

The constituent binary phase diagrams of Al-Li, Li-Mg and Al-Mg have been extensively studied. The older versions of these binary diagrams have now been updated by [82McA], [84NAY] and [82MUR] respectively.

[82McA] in their evaluation of Al-Li binary have not incorporated the findings of [80SCH, 81SCH] who had re-investigated the phase equilibria in this system using careful experimental methods in conjunction with dilatometry and elctron-probe microanalysis (EPMA). Whereas the compositions

and temperatures for the L 602°C Al + AlLi eutectic and L+ AlLi 519°C Al_2Li_3 peritectic reactions of [80SCH] are close to those recommended by [82McA], [80SCH, 81SCH] have reported the following two reactions:

L + θ($Al Li_2$) $\underset{\rightleftharpoons}{329°C}$ bcc (Li) Peritectic, and

bcc (Li) + θ ($Al Li_2$) $\underset{\rightleftharpoons}{242°C}$ θ'($Al Li_3$) Peritectoid instead of

L + Υ ($Al_2 Li_3$) $\underset{\rightleftharpoons}{335°C}$ $Al_4 Li_9$ (δ') Peritectic

L, $Al_2 Li_3$, δ'/δ at 275°C unknown, and

L $\underset{\rightleftharpoons}{175°C}$ $Al_4 Li_9$ (δ) + bcc (Li) eutectic reactions reported by [82McA].

We have adopted [80SCH]'s version of the Al-Li binary in this evaluation with the Al-Li eutectic composition of [82McA] and the sole modification that their θ($AlLi_2$) phase has been replaced by the Υ ($Al_2 Li_3$) phase of [82McA]. 82[McA] tabulate a value of 26 a/o Li for the Al-Li eutectic but their diagrams show a value of 24 a/o Li which has been assumed correct in this communication. The reason for adopting [80SCH]'s diagram is that Schürmann's group has provided the most thorough and precise studies on the Al-Li-Mg system to date and the interpretations presented in this evaluation are based on their version of the Al-Li binary which is reproduced in Fig. 1.

The Al-Mg binary diagram has several conflicting features and despite the recent assesment by [82MUR] the matter is not yet resolved. Three new contributions to the study of Al-Mg system have been made by [77SCH, 80SCH, 81SCH] as an integral part of the investigations of the Al-Li-Mg ternary system. Only [77SCH] was available at the time of [82MUR]'s assesment. Again, although it is very difficult to offer any opinion about the relative merits of the alternative versions of this system,

[80SCH]'s version of Al-Mg system has been used in this evaluation since the most thorough and significant investigation of the Al-Li-Mg ternary system is by Schürmann's group and the present interpretation of the Al-Li-Mg ternary is based on their view of the binary system. Their version of Al-Mg binary is therefore reproduced in Fig. 2. [81SCH] consider that there is good agreement between previous investigations with regard to the liquidus lines for (Al) and (Mg) and the associated composition and temperatures of

$L \underset{\rightleftharpoons}{450°C} (Al) + Al_3Mg_2 (\beta)$ eutectic, and

$L \underset{\rightleftharpoons}{437°C} (Mg) + Al_{12}Mg_{17} (\gamma)$ eutectic reactions.

The disagreements centre mainly upon the middle part of the diagram where very conflicting versions of the phase equilibria have been given. [81SCH] on the basis of their improved experimental techniques comprising thermal analysis and EPMA of quenched and slowly-cooled specimens, claim unambiguous evidence about the existence of two more phases, ζ and ε which are linked by the following three invariant reactions for which there are no counterparts in the diagram recommended by [82MUR].

L (40.8 a/o Mg) $\underset{\rightleftharpoons}{448°C}$ β (39.5 a/o Mg) + ε (42.5 a/o Mg) eutectic,

L (42.5 a/o Mg) + ζ (46.4 a/o Mg) $\underset{\rightleftharpoons}{450°C}$ ε (44.6 a/o Mg) Peritectic, and

L (44.5 a/o Mg) + γ (50.6 a/o Mg) $\underset{\rightleftharpoons}{450°C}$ ζ-Al Mg(48.1 a/o Mg) Peritectic.

β and γ clearly have the same significance as the β and γ phases of [82MUR]. ε can be identified with the R phase of [82MUR]. [80SCH], however, have not provided the crystallographic data on either of the ζ and ε phases. Further they report that the eutectic decomposition of ζ and ε is rather sluggish.

The Li-Mg binary diagram (not shown here) of [84NAY] which is the latest and exhibits the single invariant eutectic reaction

$$L \underset{\rightleftharpoons}{588°C} (Mg) + (Li)$$

has been adopted in this evaluation. Table 1 summarizes the three-phase equilibria and invariant reactions in the three binary systems as reported by different researchers, and Table 2 lists the various phases that appear in these binaries with their crystal structure and modified Pearson symbols.

THE TERNARY SYSTEM

LIQUIDUS SURFACES:

The liquidus projections of [48SHA], [77DRI] and [81SCH] exhibit reasonable agreement on the liquidus temperatures and existence of most of the solidification troughs (Figs. 3, 4, 5). However, the positions of the troughs are not coincident. [48SHA] reported the presence of two ternary eutectics, E_1 (Fig. 3) at a temperature of 419°C, and a spurious second ternary eutectic E_2 at a non-specified temperature. Besides these, they also reported six four-phase transition points. Table 3 summarizes all the reactions as originally reported by [48SHA] for this system. The solidification troughs and some isotherms as reported by [48SHA] are also shown in Fig. 3. The liquidus surface and the solidification troughs of [48SHA] do not, however, agree with the present binary phase diagrams. For example, [48SHA] considered the β-phase (Al_3Mg_2) to form via a peritectic reaction involving the liquid and the γ-phase (he considered the γ-phase to be Al_3Mg_4 which is now well established to be $Al_{12}Mg_{17}$). From the recent information on Al-Mg binary, the β-phase forms as an open

maximum compound with an eutectic on either side (Fig. 2, Table 1). Also, contrary to the only eutectic reaction (L → (Li) + (Mg)) as reported in the most recent assessment of the Li-Mg binary, [48SHA] considered the Li-Mg binary to have the phase $LiMg_2$ and a second eutectic at about 5 a/o Li and 182°C. The Al-Li binary used by [48SHA] showed AlLi as an open maximum compound and $AlLi_2$ (which is likely to be Al_2Li_3 as per the recent Al-Li binary) forming as a peritectic reaction. This agrees with the present binary diagrams [80SCH, 82MCA]. However, the results of [48SHA] do not include the peritectic compound $\delta'(Al_4Li_9)$, the binary eutectic at 2 a/o Al and 177°C of [82McA] or the peritectoid compound θ' ($AlLi_3$) of [80SCH] as accepted in this evaluation.

The portion of the liquidus surface of the Mg-rich corner of the Al-Li-Mg ternary system as determined by [77DRI] is shown in Fig. 4 and the three invariant reactions reported by them are listed in Table 3. The difference between the liquid composition and the participating phases of the eutectic reaction of [77DRI] and [48SHA] can be noted from this Table. Also [77DRI] has observed a peritectic at 436°C in place of transition point 8 (denoted by U8 in Table 3) at 434°C of [48SHA].

[81SCH] conducted an extensive investigation of the Al-Li-Mg ternary system and its associated binary systems [80SCH]. The liquidus projection of [81SCH] which is based on the 18 vertical sections studied by them is shown in Fig. 5 and the invariant reactions (a eutectic reaction and 8 four-phase transition points u_1, $u_2 \ldots u_8$) proposed by them are listed in Table 3. While there is no disagreement among [81SCH], [77DRI] and [48SHA] about the eutectic temperature of ~418°C, the eutectic composition of [81SCH] is close to that of [48SHA] and much different from [77DRI].

The participating phases, however, are in agreement with [77DRI] and as such disagree with [48SHA] due to the modified binary diagrams of [80SCH].

As seen from Table 3, the reaction sequence proposed by [81SCH], which is implicit in their liquidus projection (Fig. 5), is radically different from that of [48SHA], partly due to their more detailed determination of the isothermal contours and partly because of their revision of the binary systems, particularly Al-Mg. Some agreement with respect to certain ternary invariant reactions is, however, still apparent from Table 3.

Whereas the nature of the transition points u_1, u_2 u_3, u_4 and u_5 from the original paper of [81SCH] is quite clear, the nature of the transition points u_6, u_7 and u_8 are not very clear. It is assumed here that the transition points u_6, u_7 and u_8, in fact, represent a series of novel invariant peritectic reactions (P_1, P_2 and P_3) as indicated in Table 3. These reaction sequences in the vicinity of the binary invariant reactions are a consequence of the revision of the Al-Mg binary system by [80SCH].

A speculative liquidus diagram based on that of [81SCH] but forcing agreement with their observed data and binary diagrams is included in Fig. 6. Expanded portion of this speculative liquidus in the vicinity of Al-Mg binary invariant reactions is shown in Fig. 6a.

The solidification troughs and liquidus temperatures determined by [81SCH] are in reasonable agreement with those determined by [48SHA]. The nature of the phase fields for the formation of the ternary compound and the composition of the ternary compound are somewhat different and the

liquidus surfaces differ near the binary systems because of the use of different binary phase diagrams in the two cases. The participating phase fields of [81SCH] for the formation of the ternary phase are similar in nature to those of [77DRI] but the compositions are somewhat different. The phase fields of [81SCH] delineated by transition points U_3, U_4 and U_5 (Fig. 5) are considered to be the most accurate in this assessment since the most recent and modern techniques have been used for their characterization.

TERNARY PHASES:

[48SHA, 56LEV, 65FRI, 73DRI, 76PAD, 81SCH] have experimentally observed the presence of a true ternary phase, whereas [52JOH, 55ROW] have found no such phase. Also, the thermodynamic calculations of [77SAB] do not predict the occurrence of a ternary phase. Investigations observing an intermetallic ternary compound outnumber those not observing the compound by two to one and therefore, it is assumed in this evaluation that a ternary phase does exist. The exact composition of the ternary phase, however is not very clear. [48SHA] allotted the ternary phase a simple formula Al_2Li Mg. Although it does occur at nearly 50 a/o Al, later works of [76PAD] and [81SCH] have shown (Table 4) that the Li content is higher and the Mg content lower than this simple formula would suggest. In this evaluation, the composition of the ternary phase has been assumed to be the one due to [81SCH] which is the most recent determination, and is denoted by the symbol τ. Its crystal structure has been reported as complex cubic with a lattice parameter of 2.031 nm and with 456 atoms per unit cell [72SAM quoted by 76PAD].

[52JON], [55ROW] and [56LEV] have reported the presence of a second ternary phase $AlLi_2Mg$ (with fcc symmetry and 16 atoms per unit cell) in alloys containing Li solid solution. [55ROW] and [56LEV] both, however, attribute the X-ray diffraction patterns of this phase to a transitional, non-equilibrium phase which preceeds the rejection of AlLi from the Li solid solution. With long annealing times the $AlLi_2Mg$ phase was no longer detected. [68PAU] did not observe any such phase.

INVARIANT EQUILIBRIA:

Fig. 7 shows a speculative reaction sequence which is based on the latest versions of the constituent binaries [84NAY, 80SCH] and which allows appropriate interpretations of what is known about the invariant equilibria and the solid state triangulations.

THE SOLIDUS:

The investigation of [81SCH] is the only one which provides an almost complete solidus surface (Fig. 8) except for the extreme Li-rich end. [77DRI] have shown a section at 60% Mg and their solidus temperatures are in reasonable agreement with [81SCH]. The region of Fig. 8 in the vicinity of 50-65 a/o Al and 15-0 a/o Li is expanded in Fig. 8a to show the ζ(Al Mg) and Al_xMg_y phase fields of [81SCH]. The solid-solubility limits are quite apparent from these diagrams.

SOLID-SOLID PHASE EQUILIBRIA:

Isothermal sections based on experimental works of several investigators are presented in Fig. 9 to 25 and those calculated from thermodynamic data are presented in Fig. 26 and 27. A strict comparison cannot always

be made between the diagrams as they are not all at the same temperature but these diagrams may still be used to check the compatibility of the investigators' results.

Isothermal sections of [80SCH], [77DRI] and [56LEV] at 400°C (Fig. 10-12) show excellent agreement for the compositional limits of the (Mg) solid solution, [(Mg) + (Li)] and (Li) solid-solution phase fields. The data of [52JON] and [50FRO] at 371°C (Fig. 13, 14) and of [55ROW] at 375°C (Fig. 15) also confirm the data at 400°C. If $LiMg_2$ phase of [48SHA] is considered to be actually (Li) solid-solution then the data of [48SHA] at 400°C (Fig. 9) are also in good agreement with other investigators.

Isothermal sections of [81SCH], [56LEV] and [76PAD] at 300°C (Fig. 16-18) also show good agreement for the compositional limits of the (Mg) solid-solution, [(Mg) + (Li)] and (Li) solid solution phase fields. The data of [52JON] at 260°C (Fig. 19) are also consistent.

Isothermal sections of [80SCH], [55ROW], [56LEV] and [77DRI] at 200°C (Fig. 20-23) again show good agreement for the compositional limits of the (Mg), [(Mg) + (Li)] and (Li) solid solution phase fields. The isothermal sections at 100°C (not shown) are quite similar to those at 200°C with the respective phase fields being slightly smaller than those at 200°C.

Most researchers agree that the solubility of Li in Mg is almost constant at about 18 a/o Li in the region 200-400°C. The ternary diagrams also show good agreement with the binary Al-Mg system for the solubility of Al in Mg.

As pointed out earlier, the existence of the ternary phase Al_2Li Mg has been verified by several investigators but the reported compositions

vary and the second ternary phase $AlLi_2Mg$ has been identified to be a transitional, non-equilibrium phase.

The large ternary solubility of the $Al_{12}Mg_{17}$ phase has been verified by [48SHA] (his Al_3Mg_4 phase is actually $Al_{12}Mg_{17}$), [SCH80], [76PAD] and [56LEV]. The ternary solubility of Al_3Mg_2 phase as reported by [80SCH] and which has been assumed to be most accurate is much smaller than that of [48SHA]. The presence of ζ-AlMg phase in the ternary system has been indicated by [48SHA], [80SCH] and [56LEV]. However, the existence of this phase as a separate equilibrium compound has not been indicated by [82MUR]. Both [48SHA] and [80SCH] indicated the existence of Al_4Mg_3 (designated ε by [80SCH]) phase at temperatures of 400°C or above contrary to the findings of [82MUR] who have reported the formation of this binary compound Al_4Mg_3 (designated as R-phase by them) via a peritectoid reaction at about 370°C. According to [80SCH], Al_4Mg_3 phase forms via a peritectic reaction at 450°C. [71MIK] have also demonstrated the existence of this phase (ε or R) in Al-Mg binary alloys which were annealed for one week at 380°C. The temperature range for the existance of this phase still remains in doubt. We have tentatively assumed the latest information as provided by [80SCH] on the Al-Mg binary system to be the most correct as mentioned earlier. However, further experimental clarification is required.

The four phases, AlLi, Al_2Li Mg, $Al_{12}Mg_{17}$, and Al_3Mg_2, whose presence has been verified by [48SHA], [80SCH], [56LEV] and [73DRI] are reported to be in equilibrium with (Al) solid solution. [65FRI] have not reported the

presence of $Al_{12}Mg_{17}$ phase, but their analysis was not extensive in the region where (Al) + $Al_{12}Mg_{17}$field would occur, and as a result they might have overlooked or missed this phase.

The (Al) solid solution phase boundary determined by [73DRI] at 430°C, by [81SCH] at 400°C and by [65FRI] at 440°C (Fig. 24, Fig. 10 and Fig. 25) are in reasonable agreement. These results also agree reasonably well with the solubility limits for the Al-Mg and Al-Li binary alloys [80SCH]. The (Al) solid solution region of [48SHA] (Fig. 9) is larger and that of [56LEV] (Fig. 12) is smaller than the other investigations. The (Al) solid solution phase boundary positions of [81SCH] and [56LEV] at 300°C and 200°C are in reasonable agreement.

The extent of the Al Li compound at 400°C is shown in Figs. 9, 10 and 12, and at 300°C is shown in Figs. 16 and 18. [80SCH] and [76PAD] have both reported considerable ternary solubility for this phase, reaching a concentration of about 10 a/o Mg as shown in Figs. 10, 16, 18, 20. [56LEV] and [48SHA] have suggested lower Mg-concentrations for this phase as shown in Figs. 9, 12, 17 and 21.

Very little is known about the Al-Li-Mg ternary system at higher Li-concentrations perhaps due to the extreme reactivity of lithium. [56LEV] have reported very little ternary solubility for Al Li_2 (assumed Al_2Li_3 here). There are no reports on the ternary solubility of either the $\delta(Al_4Li_9)$ phase of [82McA] or the $\theta'(Al\ Li_3)$ phase of [80SCH]. The reactivity of lithium-rich alloys makes experimental work in the Li-rich region of the Al-Li-Mg system very difficult [56LEV].

The thermodynamic predictions of [77SAB] are of some interest. Their 400°C isotherm is included in Fig. 26 which shows that liquid is present at Li concentrations less than 50 at %. This is contrary to the work of [81SCH] who have shown that only solids are present in this area below temperatures of about 418°C. Further, the calculations of [77SAB] do not predict the occurrence of the ternary phase Al_2Li Mg (or $Al_6Li_3Mg_2$).

The calculated isotherm at 375°C, which is shown in Fig. 27, predicts equilibrium between (Mg) solid solution, AlLi and Al_2Li_3. This is most interesting since none of the experimental investigations have reported or even suggested the existence of such a phase field.

Conclusion

It is considered that the works of [81SCH] and [80SCH] are fairly accurate representations of the Al-Li-Mg ternary system. Much of their work is substantiated by previous investigations on various aspects of Al-Li-Mg ternary alloys. The Li-rich corner of the ternary phase diagram remains undetermined but these alloys have limited practical significance because of their reactivity. Also, the area of the phase diagram between Al_3Mg_2 and $Al_{12}Mg_{17}$ remains in doubt largely because of the uncertainty of the Al-Mg binary diagram in this area. Work is currently in progress in our labs to establish this portion of the Al-Mg binary system.

Recommendation for Further Work

1. The ternary phase diagram between the $Al_{12}Mg_{17}$ and Al_3Mg_2 phases needs more work to determine if the phase AlMg (ζ-phase) exists. Also, ternary solubility of the Al_6Mg_3 phase needs to be determined.

2. More work is required to confirm the structure and composition of the ternary compound.
3. There is some doubt concerning the phase relationships at the Li-rich corner of the ternary Al-Li-Mg system. This needs to be studied.

Table 1

Reaction Symbol	Reactions (Ref. [82McA])	Reactions (Ref. [80SCH])
Al-Li System (compositions in a/o Li)		
e_1	L(24 a/o) 600°C α^*(14 a/o) + β^*(45 a/o)	- same -
P_1	β(55 a/o) + L(77 a/o) 520°C γ^*(60 a/o)	- same -
P_2	L(90 a/o) + γ^*(60 a/o) 335°C δ'^*(69 a/o)	L(90 a/o) + θ^*(74.0 a/o) 329°C Li(87.0 a/o)
?	γ(60 a/o) δ/δ'(69 a/o) L(95 a/o) 275°C	Li(87.0 a/o) + θ^*(74.0 a/o) 242°C Al $Li_3(\theta')^*$(82.2 a/o)
e_2	L(98 a/o) 177°C δ(69 a/o) + bcc Li(100 a/o)	

$^*\alpha$ = (Al), β = Al Li, γ = θ = Al_2Li_3, δ/δ' = Al_4Li_9, θ' = $Al Li_3$.

Al-Mg System (Composition in a/o Mg)

Liquid Solid Equilibria

e_1	L(38 a/o) 450°C (Al) (18.6 a/o) + β(38.5 a/o)	- same -
e_2	L(69 a/o) 437°C γ (62.3 a/o) + (Mg) (88.5 a/o)	- same -
e_3	L(41.2 a/o) 450°C β(40.3 a/o) + γ(45 a/o) e_3	L(40.8 a/o) 448°C β(39.5 a/o) + ε(42.5 a/o)
P_1		L(42.5 a/o) + ζ(46.4 a/o) 450°C ε(44.6 a/o)
P_2		L(44.5 a/o) + γ(50.6 a/o) 452°C ζ(48.1 a/o)

Solid-Solid Equilibria:

Pd_1	β(40.3 a/o) + γ(52 a/o) 370°C R(42a/o)	
ed_1	R(42 a/o) 320°C β(40.3 a/o) + γ(55 a/o)	

β = Al_3Mg_2, γ = $Al_{12}Mg_{17}$, R ≡ ε = $Al_{30}Mg_{23}$ ~ $Al_{31}Mg_{22}$(~Al_4Mg_3), ζ ~ Al Mg

Li-Mg System [84NAY] (Composition in a/o Li)

e_1 L(23.0 a/o) 588°C Mg(17.0 a/o) + Li(24.5 a/o)

TABLE 2: Phases and their crystal structure in Al-Li-Mg Ternary System and its Constituent Binaries.

Phase/(Temp.°C)	Symbols used in literature/Ref.	Symbols adopted here	Approximate Composition (at/o)	Pearson Symbol/ Space Group	Prototype	Lattice Parameters in nm a	b	c	Comments
Al-Li Binary System									
Al-Solid Solution < 660.5°C	α[82McA]	(Al)	0-15 Li	cF4/ $Fm\bar{3}m$	Cu	0.40495*	-	-	*At 0 at/o Li
AlLi < 700°C	β[82McA] η[80SCH]	η	45-55 Li	cF16/ $Fd\bar{3}M$	NaTl	0.637**	-	-	**At 50 a/o Li
Al_2Li_3 < 520°C	γ[82McA] θ[80SCH]	θ	60-61 Li	hR5/ $R\bar{3}m$	Bi_2Te_3	0.4508	-	1.426	[80SCH] assumed θ=Al Li_2. Here it has been assumed to be Al_2Li_3
Al_4Li_9† < 275°C	δ[82McA]	-	Line Compound at 69.2 Li	mC2 6/ B2/m	-	1.91551	0.54288	0.44988	β = 107.67
Al_4Li_9† (275-330°C)	δ'[82McA]	-	69.2 Li	unclassified	-	-	-	-	†phases ignored in this evaluation
AlLi†† < 242°C	θ'[80SCH]	θ'	82.5-85.1	-	-	-	-	-	††Instead of Al_4Li_9 phase of [82McA] $AlLi_3$ phase of [80SCH] has been adopted in this evaluation
Li-Solid(a) Solution < 180.6°C	(Li)[82McA]	-	100.0 Li	C I2/ IM 3m	W	-	-	-	

TABLE 2: (Continued)

Phase/(Temp.°C)	Symbols used in literature/Ref.	Symbols adopted here	Approximate Composition (at/o)	Pearson Symbol/ Space Group	Prototype	Lattice Parameters in nm a	b	c	Comments
Al-Li Binary System									
Li Solid[a] solution < 329°C	λ[80SCH]	(Li)	87.0-100 Li	-	-	-	-	-	[a] Li Solid Solution due to [80SCH] has been adopted here
Al_3Li Metastable	α'[82McA]	-	-	CP4/ $Pm\bar{3}m$	$AuCu_3$	0.4010	-	-	
Li-Mg Binary System									
Mg-Solid Solution	δ[80SCH]	(Mg)	0-17 Li	hP2/ P63/mmc	Mg	0.32093	-	0.52107	at 0 a/o Li
Li-Solid Solution	λ[80SCH]	(Li)	24.5 100 Li	C I2/ Im3m	W	0.35093	-	-	at 100 a/o Li
Li (low-temperature phase) < -201°C	(Li)	-	100 Li	h P2/ P63/mmc	Mg	-	-	-	
Al-Mg Binary System									
Al-Solid Solution	(Al)[82MUR] α[80SCH]	(Al)	0-18.6 Mg	cF4/ Fm3m	Cu	-	-	-	
Al_3Mg_2 < 450°C	β[82MUR] [80SCH]	β	38.5-40.3 Mg	cF1168/ Fd3m(07h)	γ-Cd_2N_a	2.8239± 0.0001 [65SAM]	-	-	at 39.94 a/o Mg (~1164 atoms/unit cell)
γ-Al_4Mg_3 or γ-$Mg_{32}Al_{30}$	R[82MUR] (220-272°C) ε[80SCH] (410-425°C)	R	42.0 Mg	hR53/ R3	Co Cr Mo	12.8254 ±0.0003 [68SAM]	-	21.7478 ±0.0009 [68SAM]	

TABLE 2: (Continued)

Phase/(Temp.°C)	Symbols used in literature/Ref.	Symbols adopted here	Approximate Composition (at/o)	Pearson Symbol/ Space Group	Prototype	Lattice Parameters in nm a	b	c	Comments
Al-Mg Binary System									
$Al_{12}Mg_{17}$ < 450°C	γ[82MUR]	γ	45-60.5 Mg	cI58/ I43m	-(αMn)	10.5791 [50MAK]	-	-	58.10 atoms/unit cell
Mg-Solid Solution	(Mg)[82MUR] δ[80SCH]	(Mg)	69-100 Mg 88.4-100 Mg	hP2/ P63/mmc	Mg	0.32093	-	0.52107	at 0 a/o Al
Al_3Mg_2 (Metastable)	-	-	40-58.7 Mg	Tetragonal	-	-	-	-	
-Al Mg	ζ[80SCH]	ζ	-	-	-	-	-	-	
Al-Li-Mg Ternary System									
- Al_2Li Mg or - Al_4Li Mg_2	V[81SCH]	τ1	54a/o Al + 32 a/o Li + 14 a/o Mg	Cubic	-	2.02 [56LEV]	-	-	
Al Li_3Mg Transitions)	-	-	-	Cubic	-NaTl	0.67 [56LEV]			

Table 3

TERNARY INVARIANT REACTIONS IN THE Al-Li-Mg SYSTEM

Reaction Symbol	Temperature °C	Reaction	Liquid Phase Composition (At/o) Al	Li	Mg	Remarks
[48SHA]						
E_1	419	$L \rightarrow (Mg) + LiMg_2^* + Al_2Li\,Mg$	25.0	25.0	50.0	* In view of the recent information on the binary systems, the $LiMg_2$, $Al\,Li_3$, Al_3Mg_4 and Phase II of [48SHA] should now be (Li), Al_2Li_3, $Al_{12}Mg_{17}$ and Al_3Mg_2 respectively.
E_2(spurious)	?	$L \rightarrow (Li) + Li\,Mg_2^{**} + Al\,Li_2^*$	-	-	-	
u_2	472	$L + Al_2Li\,Mg \rightarrow (Al) + Al_3Mg_4^*$	62.5	13.3	24.2	
u_3	498	$L + Al\,Li \rightarrow (Al) + Al_2Li\,Mg$	63.5	17.5	19.0	
u_4	422	$L + Li\,Mg_2^* \rightarrow Al_2Li\,Mg + Al_3Mg_4^*$	27.8	22.0	50.2	
u_5	434	$L + Al\,Li \rightarrow Al_2Li\,Mg^* + LiMg_2^*$	24.4	27.1	48.5	
u_{10}	?	$L + Al\,Li \rightarrow Al\,Li_2^* + Li\,Mg_2^*$	6.0	75.0	19.0	
u_{24}	?	$L \rightarrow Al_3Mg_4^* + (Al) + \text{Phase II}^*$	61.5	12.7	25.8	** $Li\,Mg_2$ in E_2 should perhaps be (Mg).

Table 3: (continued)

Reaction Symbol	Temperature °C	Reaction	Liquid Phase Composition (At/o) Al	Li	Mg	Remarks
[77DRI]						
E	419	$L \rightarrow (Mg) + Al\,Li + Al_{12}Mg_{17}$	23.0	16.0	16.0	→ Compare this with E_1 of [48SHA]
P_1	436	$L + (Li) \rightarrow (Mg) + Al\,Li$	12.9	20.6	66.5	→ Compare this with u_8 of [48SHA]
P_2	446	$L + Al_2Li\,Mg \rightarrow Al_{12}Mg_{17} + (Mg)$	25.0	18.25	56.75	
[81SCH]						
E	418	$L \rightarrow (Mg) + Al\,Li + Al_{12}Mg_{17}$	29.0	20.6	50.4	† $Al\,Li_2$ will be replaced by Al_2Li_3 as indicated earlier in the text.
u_1	411	$L + Al\,Li \rightarrow (Li) + Al\,Li_2$	12.6	61.0	26.4	
u_2	436	$L + (Li) \rightarrow (Mg) + Al\,Li$	23.9	29.3	46.8	
u_3	464	$L +$ Ternary V-phase†† $\rightarrow Al\,Li + Al_{12}Mg_{17}$	39.8	20.1	40.1	
u_4	536	$L + Al\,Li \rightarrow Al +$ Ternary V-phase††	66.0	19.4	14.6	
u_5	483	$L +$ Ternary V-phase†† $\rightarrow (Al) + Al_{12}Mg_{17}$	61.5	10.8	27.7	†† Ternary V-phase of [81SCH] as discussed in a later section is the ternary compound with an approximate chemical formula - $Al_8Li_3Mg_2$ as accepted in the present evaluation.
$u_6(P_1)$	458	$L + (Al) + Al_{12}Mg_{17} \rightarrow Al_3Mg_2$*	60.5	6.0	33.5	
$u_7(P_2)$	451	$L + Al_{12}Mg_{17} \rightarrow Al_3Mg_2 + Al\,Mg$*	58.6	2.7	39.9	
$u_8(P_3)$	449	$L + Al\,Mg \rightarrow Al_4Mg_3 + Al_3Mg_2$*	58.3	1.0	40.7	

* following convention of [82WES].

Table 4 The Ternary Phase τ in the Al-Li-Mg System

Symbol	Formula	Actual Formula	Composition (at/o) Al	Li	Mg	Lattice Spacing nm	Ref.
X	Al_2LiMg	$Al_2Li\ Mg$	50.0	25.0	25.0	-	[48SHA]
-	Al_2LiMg	$\triangleq Al_6Li_4Mg_3$	46.0	31.0	23.0	2.02	[56LEV]
-	Al_2LiMg	$\triangleq Al_9Li_5Mg_2$	55.0	32.0	13.0	2.031	[76PAD]*
V	Al_2LiMg	$Al_8Li_8Mg_2$	53.5	33.0	13.5	-	[81SCH]**

*[76PAD] quotes [72SAM] as giving the ternary phase a cubic symmetry with 456 atoms per unit cell.

**In this evaluation, the composition of the ternary phase assumed is the one due to [81SCH] and its symbol is denoted by τ.

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Figure Captions

Fig. 1. Al-Li Binary System (80SCH, 81SCH).

Fig. 2. Al-Mg Binary System (77SCH, 80SCH, 81SCH)

Fig. 3. Liquidus Surface of the Al-Li-Mg Ternary as Determined by [48SHA]

Fig. 4. Liquidus Troughs as Determined by [77DRI]

Fig. 5. Liquidus Surface of the Al-Li-Mg Ternary as Determined by [81SCH]

Fig. 6. Speculative Liquidus for the Al-Li-Mg Ternary Based on that of [81SCH]

Fig. 6a. Expanded Portion of the Speculative Liquidus (Fig. 6) in the Vicinity of Al-Mg Binary Reaction

Fig. 7. Speculative Reaction Sequence for the Al-Li-Mg System based upon [80SCH]

Fig. 8. Solidus of Al-Li-Mg Ternary [81SCH]

Fig. 8a. Solidus in the Region 50-65 At% Al [81SCH]

Fig. 9. Isothermal Section at 400 C after [48SHA]

Fig. 10. Isothermal Section at 400 C after [80SCH]

Fig. 11. Isothermal Section at 400 C after [77DRI]

Fig. 12. Isothermal Section at 400 C after [56LEV]

Fig. 13. Isothermal Section at 371 C after [52JON]

Fig. 14. Isothermal Section at 371 C after [50FRO]

Fig. 15. Isothermal Section at 375 C after [55ROW]

Fig. 16. Isothermal Section at 300 C after [81SCH]

Fig. 17. Isothermal Section at 300 C after [56LEV]

Fig. 18. Isothermal Section at 300 C after [76PAD]

Fig. 19. Isothermal Section at 260 C after [52JON]

Fig. 20. Isothermal Section at 200 C after [80SCH]

Fig. 21. Isothermal Section at 200 C after [55ROW]

Fig. 22. Isothermal Section at 200 C after [56LEV]

Fig. 23. Isothermal Section at 200 C after [77DRI]

Fig. 24. Isothermal Section at 430 C after [73DRI]

Fig. 25. Isothermal Section at 440 C after [65FRI]

Fig. 26. Computed 400 C Isotherm of the Al-Li-Mg System after [77SAB]

Fig. 27. Computed 375 C Isotherm of the Al-Li-Mg System after [77SAB]

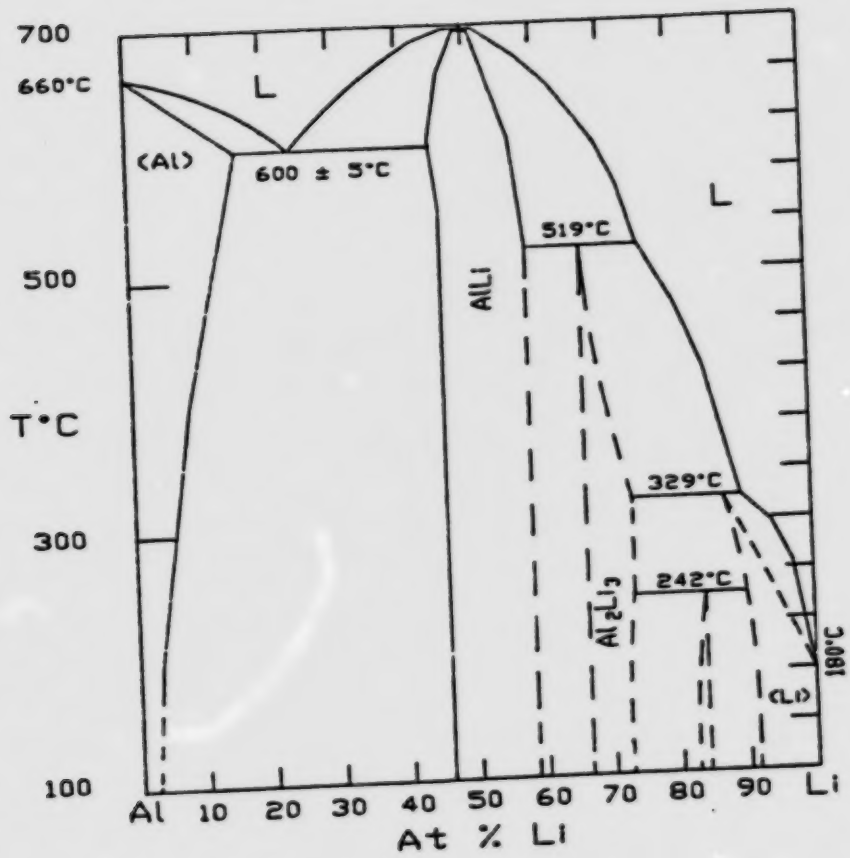

700
660°C
L
(Al)
600 ± 5°C
519°C
AlLi
L
500
T°C
329°C
300
242°C
180°C
100
Al
10
20
30
40
50
60
70
80
90
Li
At % Li

Fig. 1

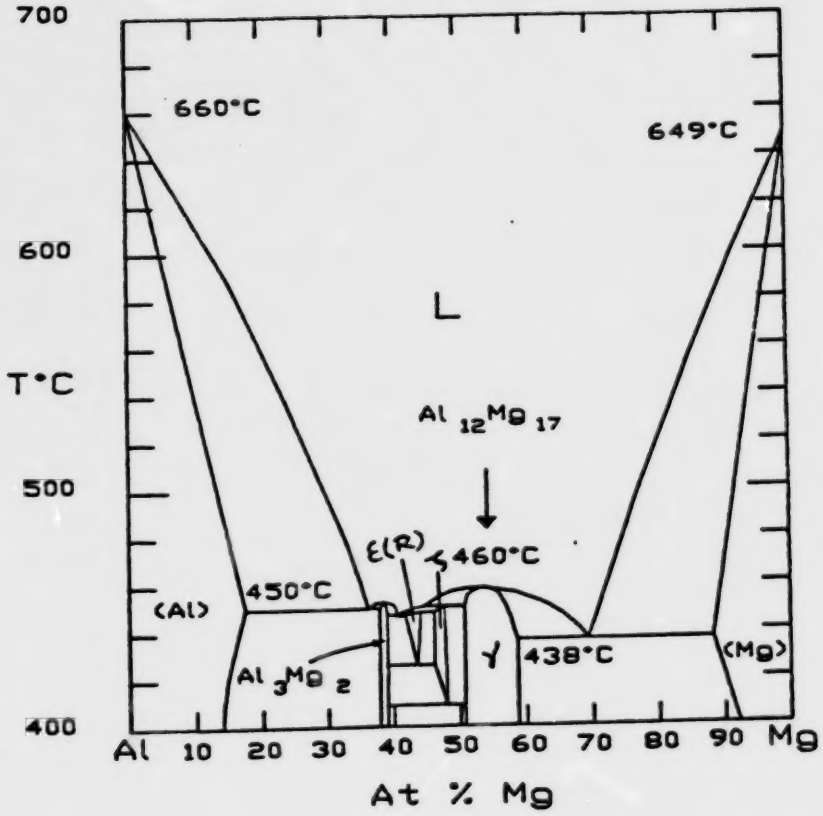
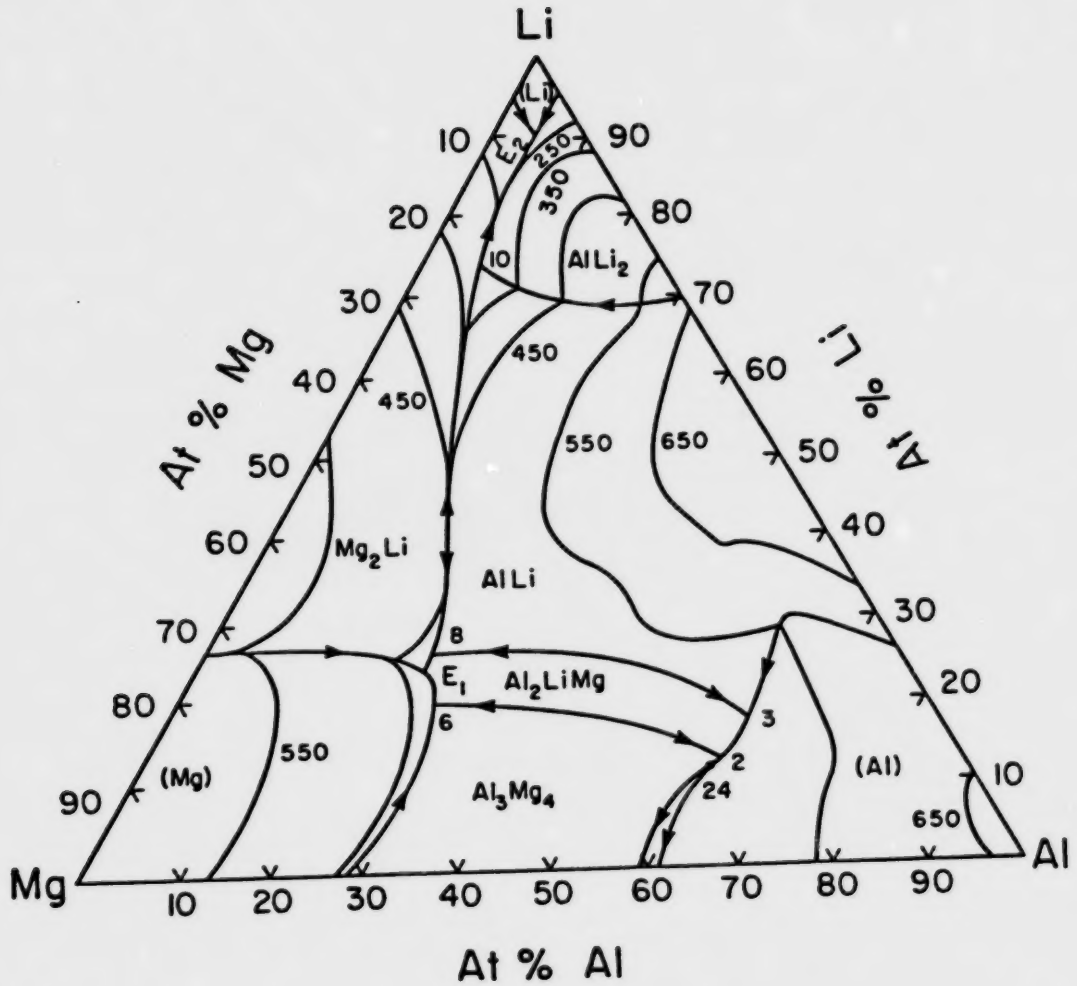

700
600
500
400
T°C
660°C
649°C
L
Al 12Mg 17
460°C
ε(R)
450°C
(Al)
γ
438°C
(Mg)
Al 3Mg 2
Al 10 20 30 40 50 60 70 80 90 Mg
At % Mg

Fig. 2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(Li)
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350
10
AlLi2
450
450
550
650
Mg2Li
AlLi
8
E1
Al2LiMg
6
3
2
24
(Mg)
550
Al3Mg4
(Al)
650
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90

Ftg 3

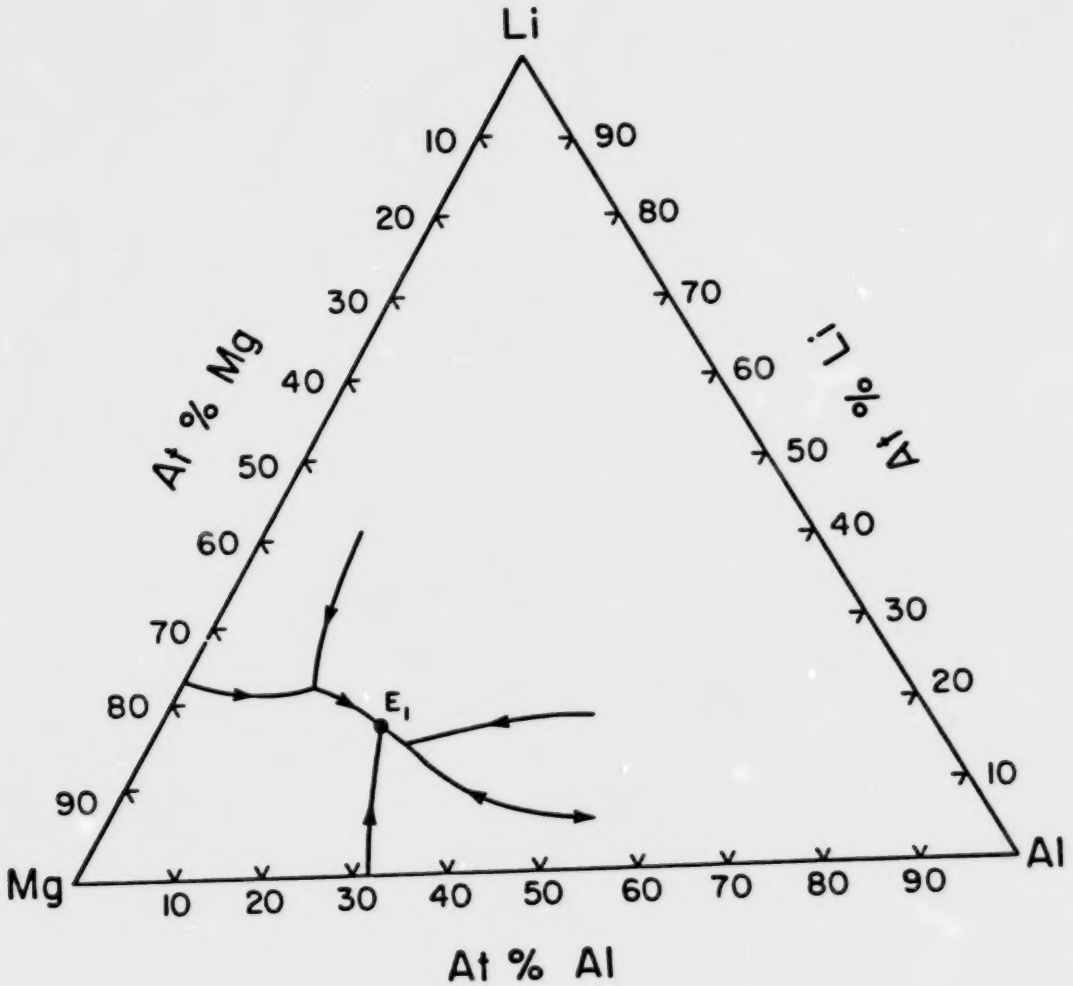


Fig. 4

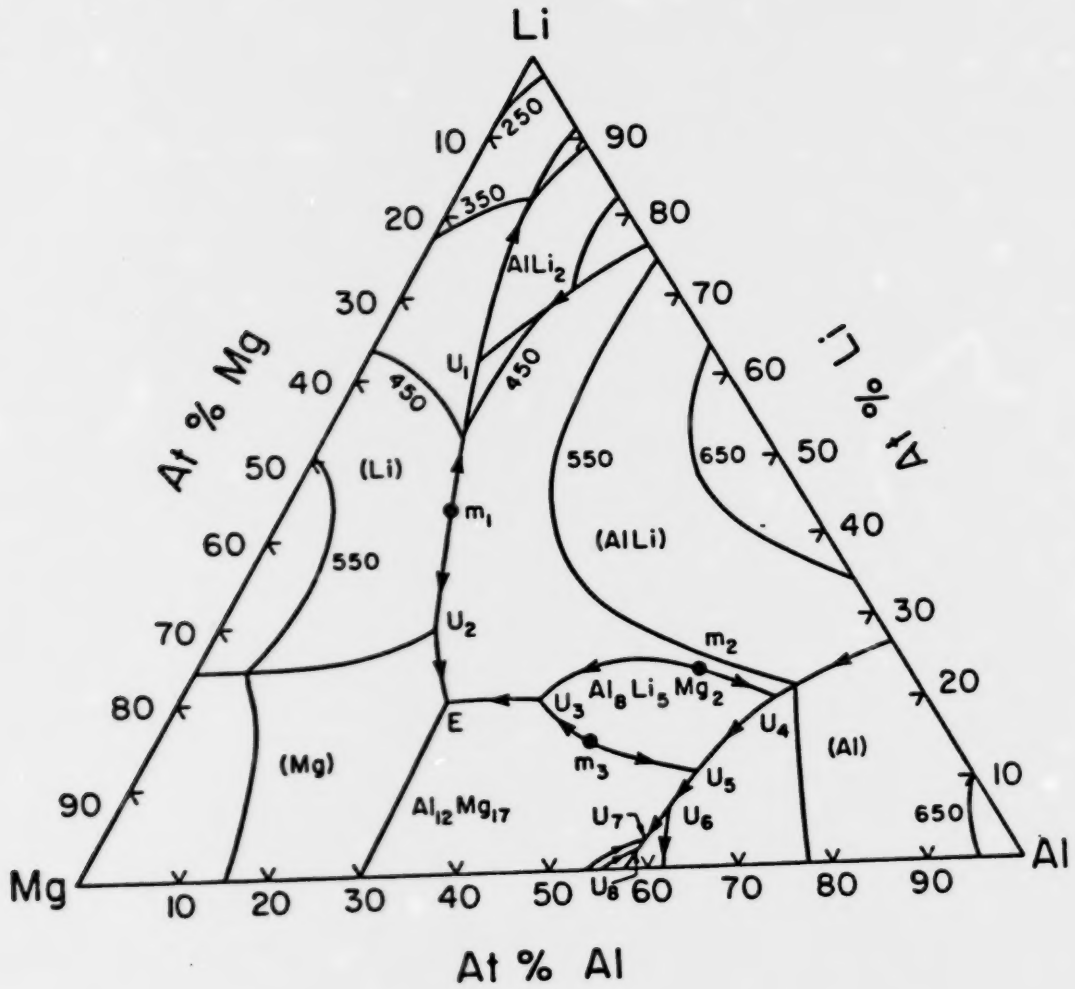

Li
Mg
Al
At % Mg
At % Al
At % Li
10
20
30
40
50
60
70
80
90
250
350
450
550
650
AlLi2
U1
U2
U3
U4
U5
U6
U7
U8
m1
m2
m3
E
(Li)
(AlLi)
(Mg)
(Al)
Al8Li5Mg2
Al12Mg17

Fig. 5

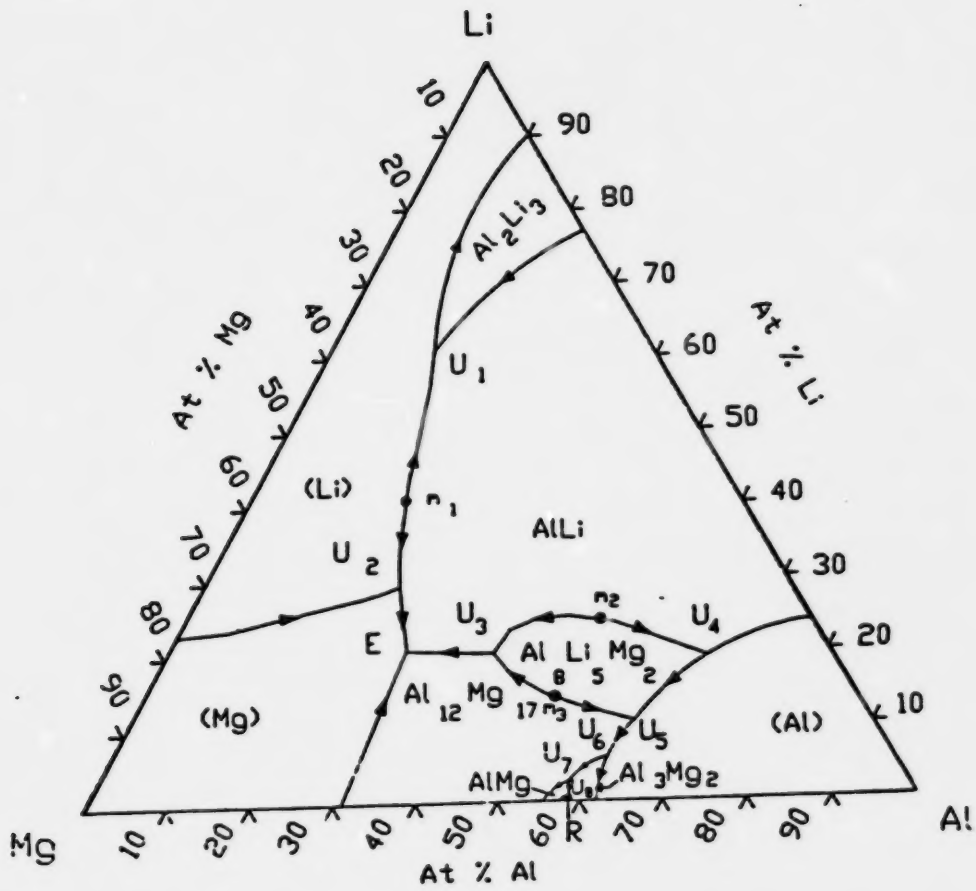

Li
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90
(Li)
(Mg)
(Al)
AlLi
Al_2Li_3
$Al_{12}Mg_{17}$
Al_3Mg_2
AlMg
$Al_2Li_3Mg_2$
U_1
U_2
U_3
U_4
U_5
U_6
U_7
U_8
n_1
n_2
n_3
E
R

Fig. 6

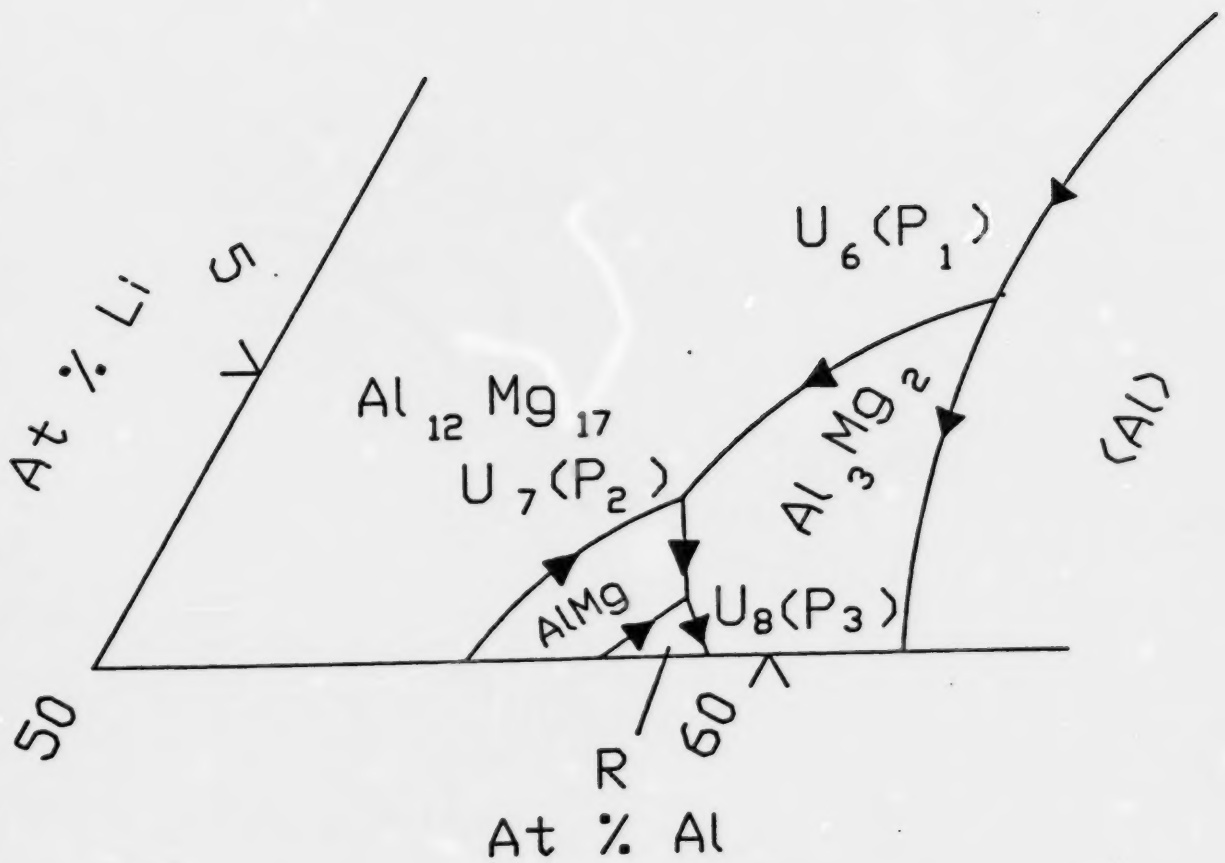
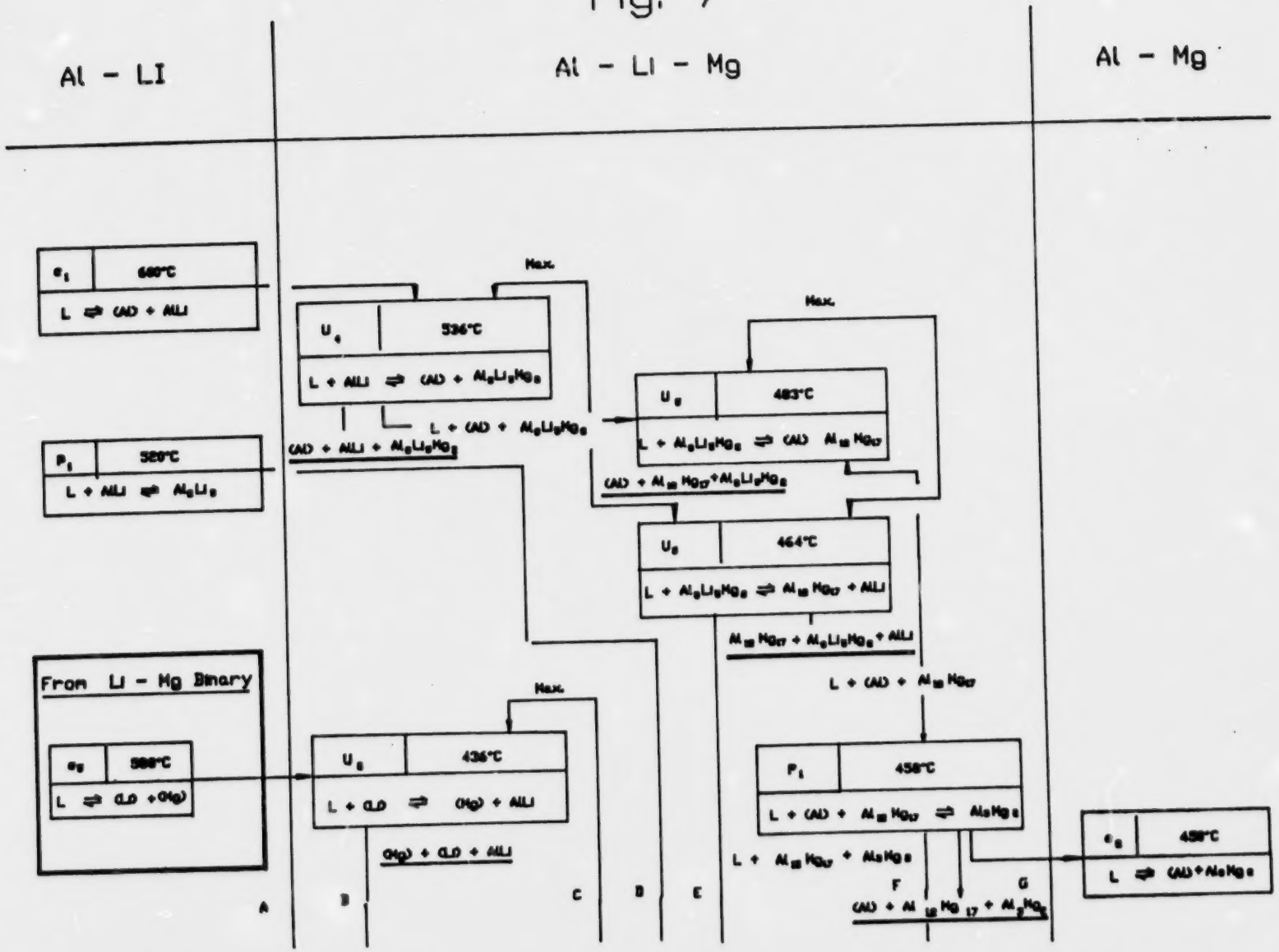
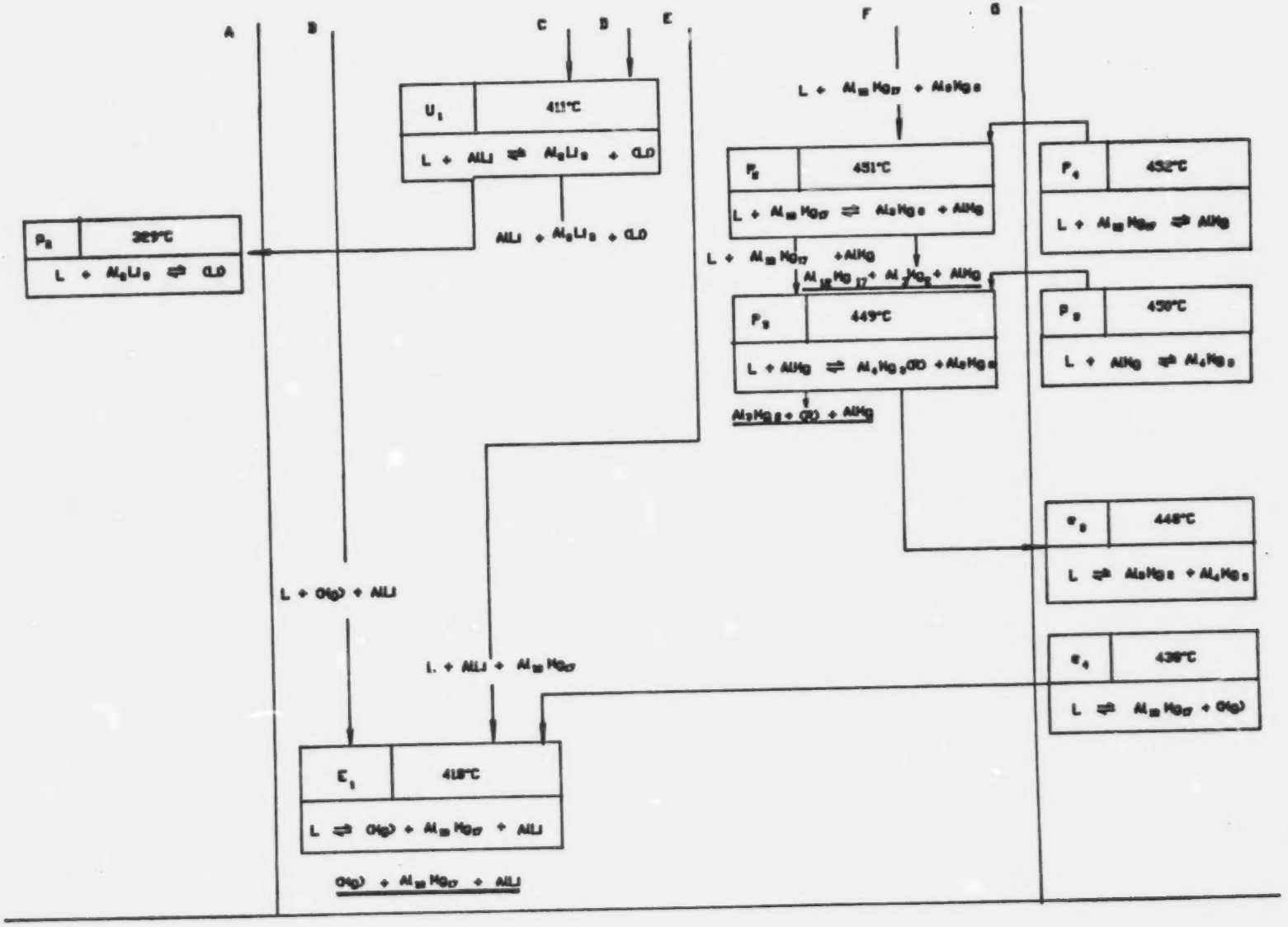


Fig. 6a

Fig. 7


Al - LI
Al - LI - Mg
Al - Mg
e1 600°C
L ⇌ (Al) + AlLi
U4 536°C
L + AlLi ⇌ (Al) + Al6Li3Mg6
L + (Al) + Al6Li3Mg6
(Al) + AlLi + Al6Li3Mg6
P1 520°C
L + AlLi ⇌ Al6Li3
Max.
U5 483°C
L + Al6Li3Mg6 ⇌ (Al) + Al12Mg17
(Al) + Al12Mg17 + Al6Li3Mg6
U6 464°C
L + Al6Li3Mg6 ⇌ Al12Mg17 + AlLi
Al12Mg17 + Al6Li3Mg6 + AlLi
L + (Al) + Al12Mg17
From Li - Mg Binary
e6 588°C
L ⇌ CLD + (Mg)
U6 436°C
L + CLD ⇌ (Mg) + AlLi
(Mg) + CLD + AlLi
P4 458°C
L + (Al) + Al12Mg17 ⇌ Al3Mg2
L + Al12Mg17 + Al3Mg2
e8 458°C
L ⇌ (Al) + Al3Mg2
(Al) + Al12Mg17 + Al3Mg2
A
B
C
D
E
F
G


A
B
C
D
E
F
G
U1 411°C
L + AlLi ⇌ Al2Li2 + CLD
AlLi + Al2Li2 + CLD
P2 389°C
L + Al2Li2 ⇌ CLD
L + Al12Mg17 + Al3Mg2
P3 451°C
L + Al12Mg17 ⇌ Al3Mg2 + AlMg
P4 452°C
L + Al12Mg17 ⇌ AlMg
L + Al12Mg17 + AlMg
Al12Mg17 + Al3Mg2 + AlMg
P5 449°C
L + AlMg ⇌ Al6Mg9(D) + Al3Mg2
Al3Mg2 + D(s) + AlMg
P6 450°C
L + AlMg ⇌ Al6Mg9
e5 448°C
L ⇌ Al3Mg2 + Al6Mg9
e4 438°C
L ⇌ Al12Mg17 + D(s)
L + D(s) + AlLi
L + AlLi + Al12Mg17
E1 418°C
L ⇌ D(s) + Al12Mg17 + AlLi
D(s) + Al12Mg17 + AlLi

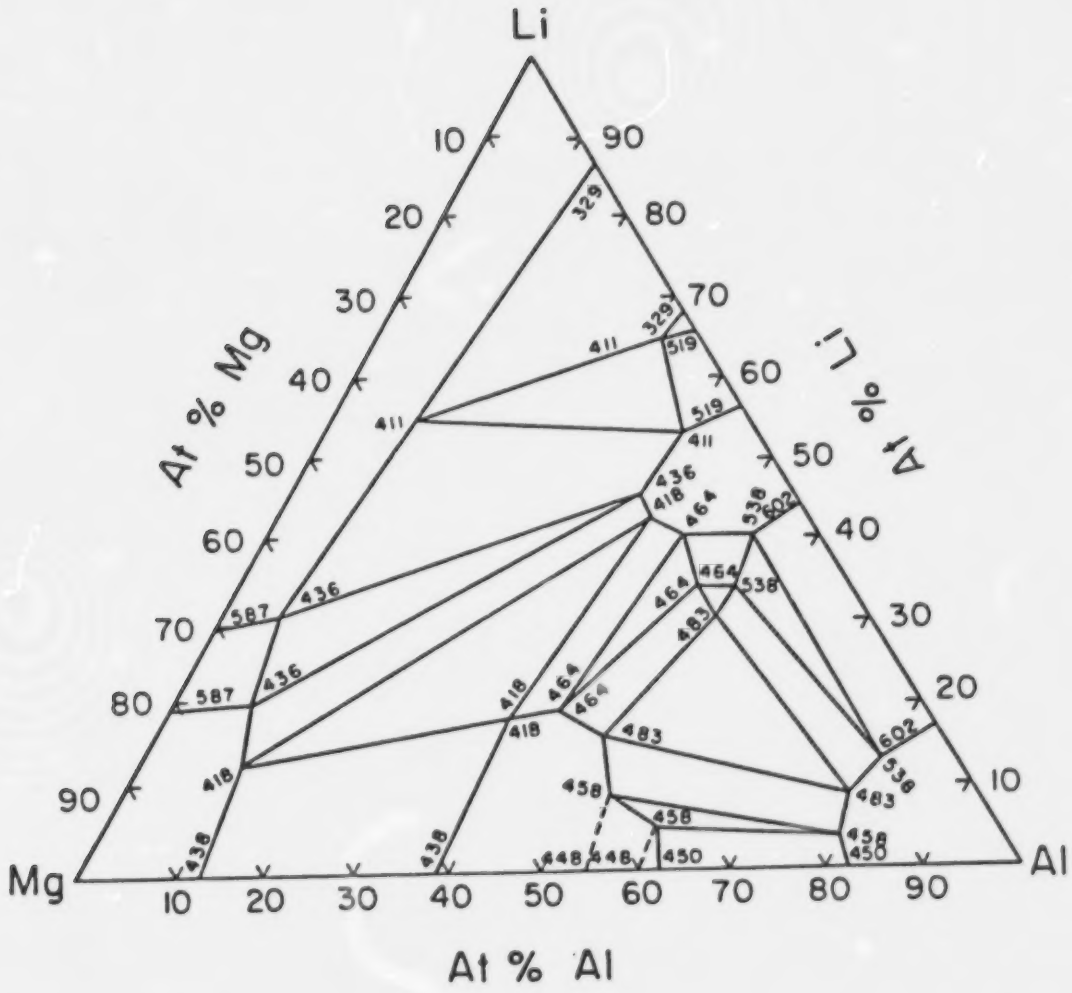

Li
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90
329
411
519
436
418
464
538
602
587
483
458
448
450
438

Fig. 8

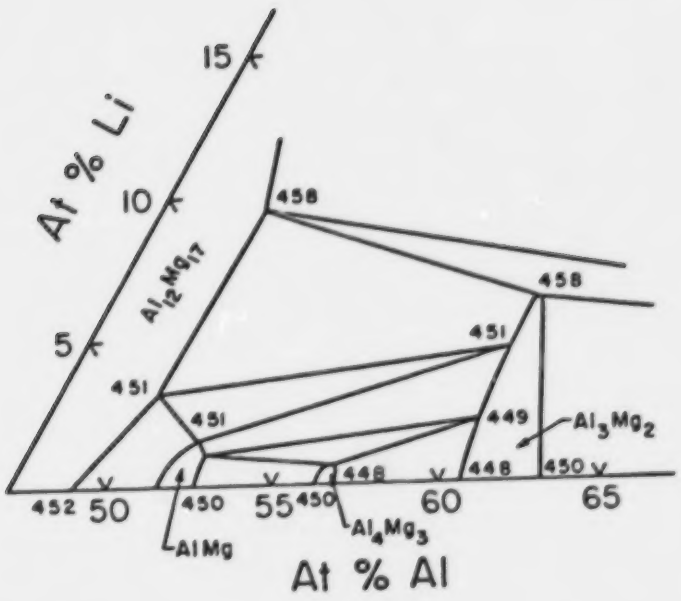

15
10
5
At % Li
$Al_{12}Mg_{17}$
458
458
451
451
451
449
Al_3Mg_2
448
448
450
452
50
450
55
450
60
65
AlMg
Al_4Mg_3
At % Al

Fig. 8a

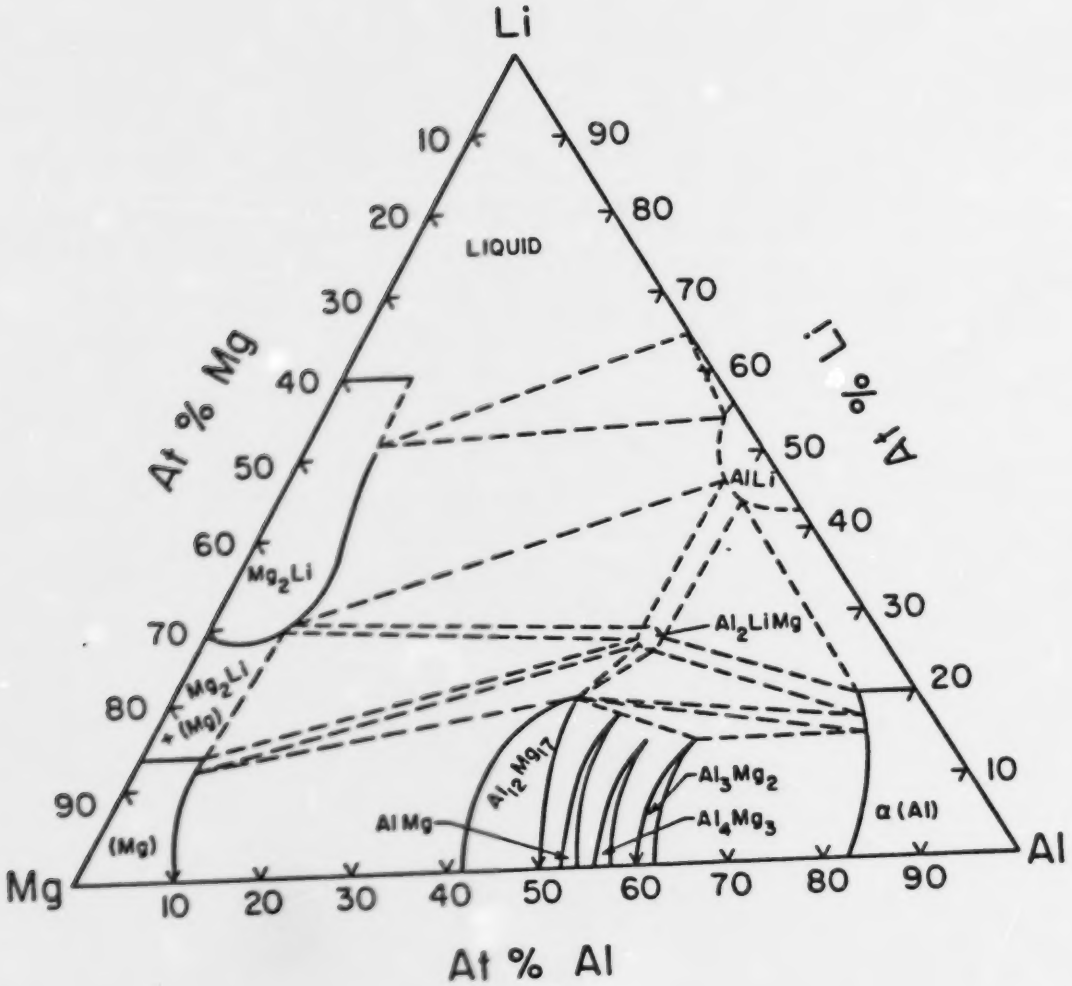

Li
LIQUID
At % Mg
At % Li
At % Al
Mg
Al
AlLi
Al_2LiMg
Mg_2Li
Mg_2Li + (Mg)
(Mg)
AlMg
$Al_{12}Mg_{17}$
Al_3Mg_2
Al_4Mg_3
α (Al)
10
20
30
40
50
60
70
80
90

Fig. 9

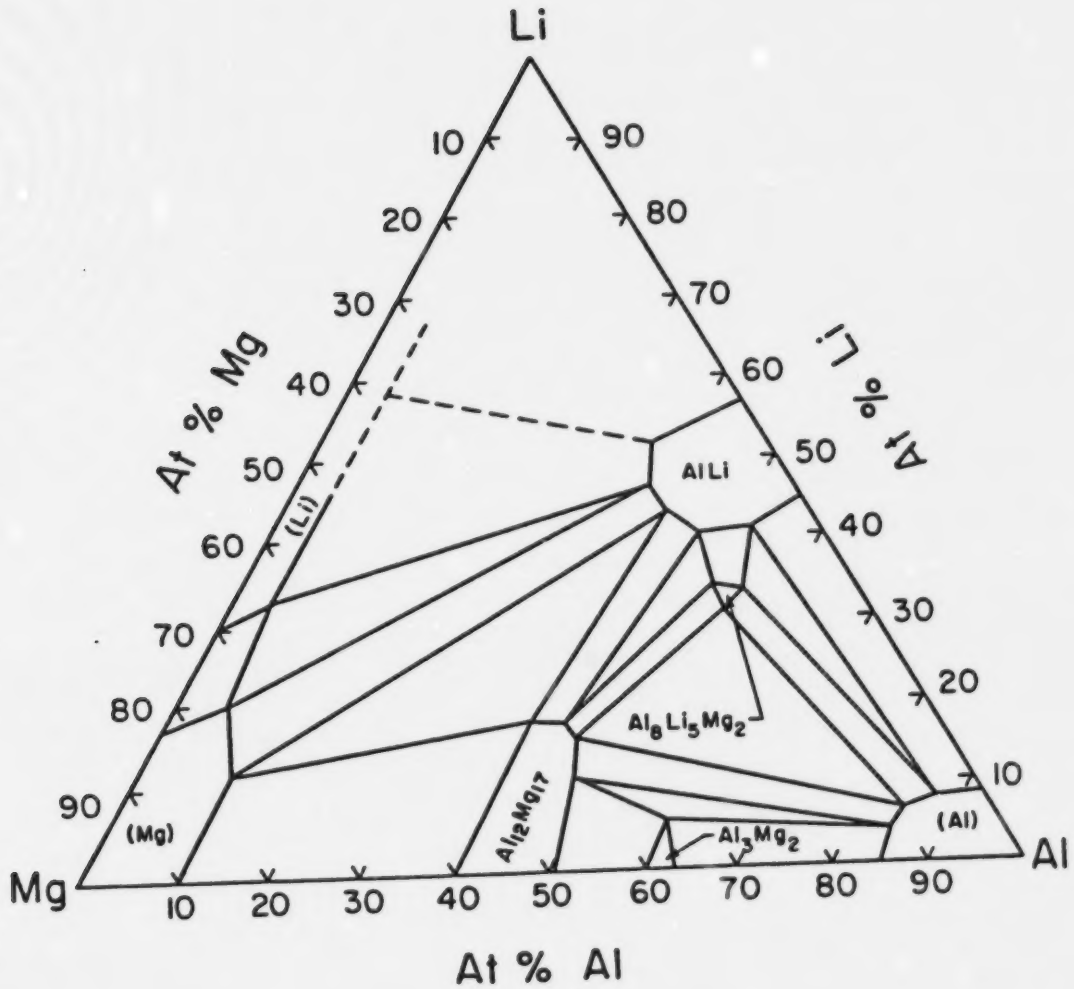

Li
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90
(Li)
(Mg)
(Al)
AlLi
$Al_8Li_5Mg_2$
$Al_{12}Mg_{17}$
Al_3Mg_2

Fig. 10

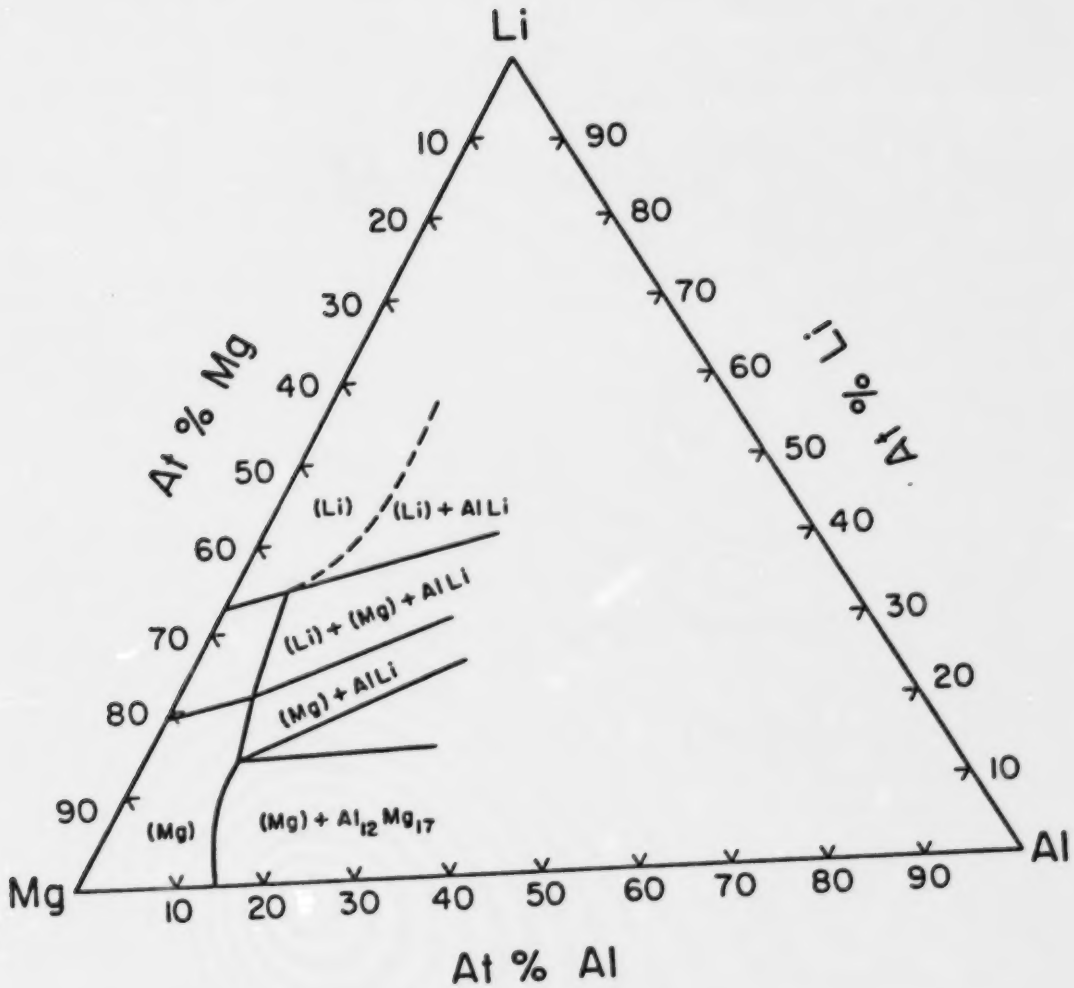
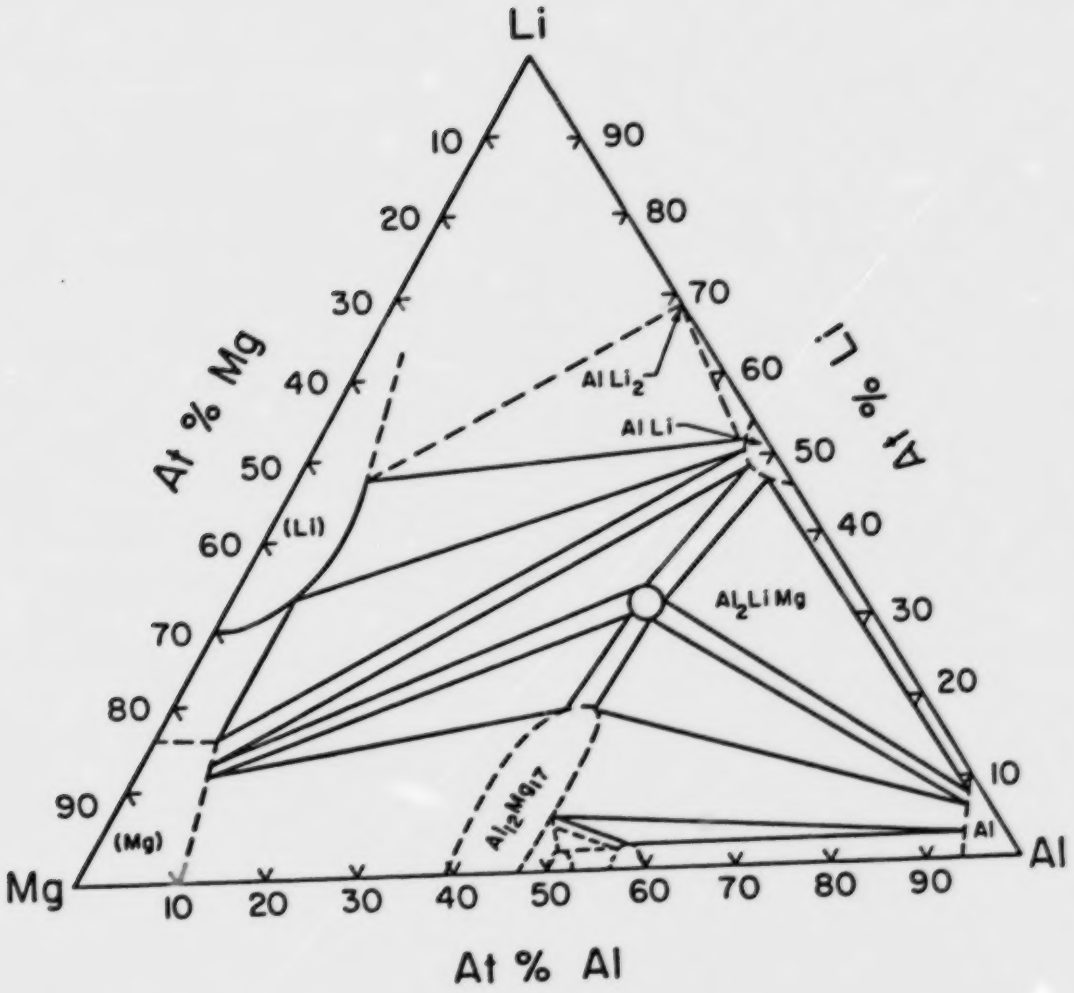
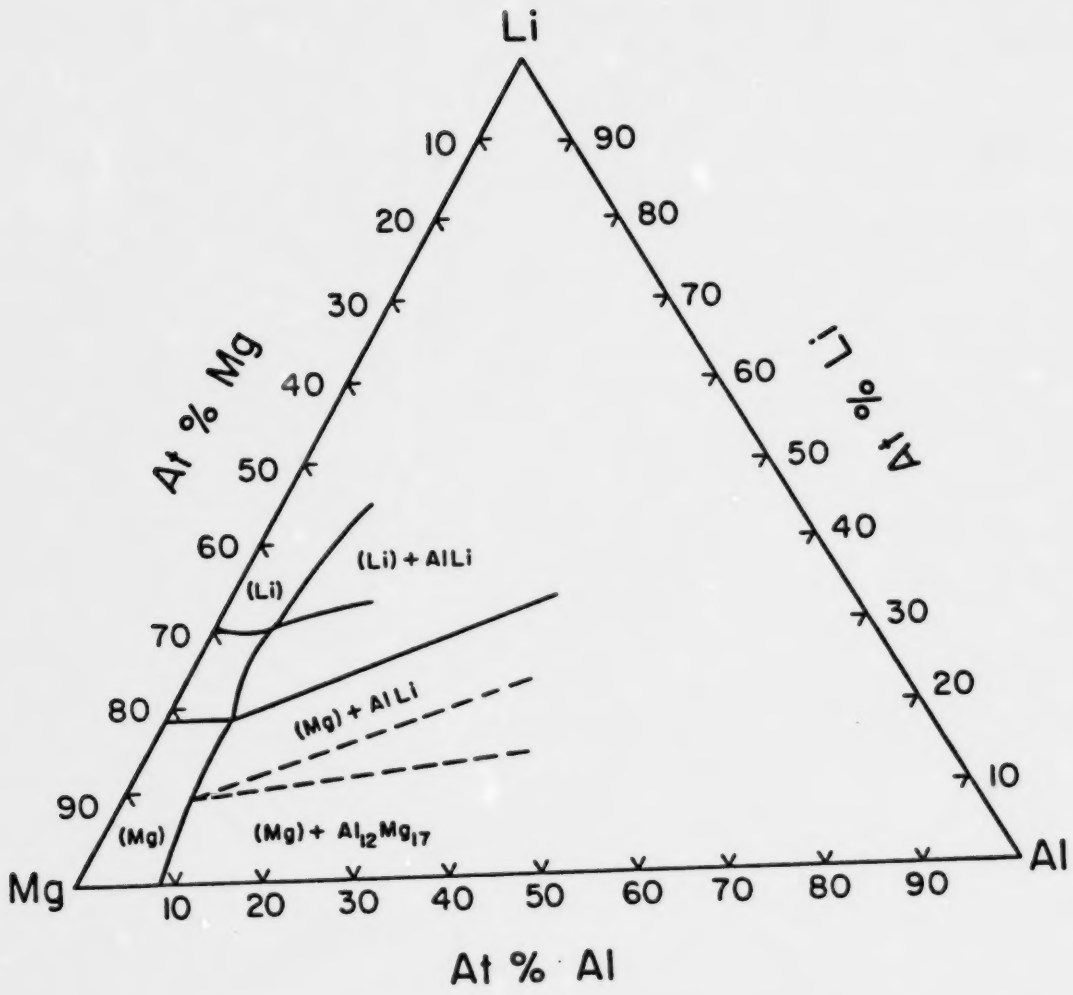

Li
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90
(Li)
(Li) + AlLi
(Li) + (Mg) + AlLi
(Mg) + AlLi
(Mg)
(Mg) + Al12Mg17

Fig. 11


Li
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90
(Li)
(Mg)
Al Li2
Al Li
Al2LiMg
Al12Mg17
Al

Ftg. 12


Li
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90
(Li)
(Li) + AlLi
(Mg) + AlLi
(Mg)
(Mg) + $Al_{12}Mg_{17}$

Ftg. 13

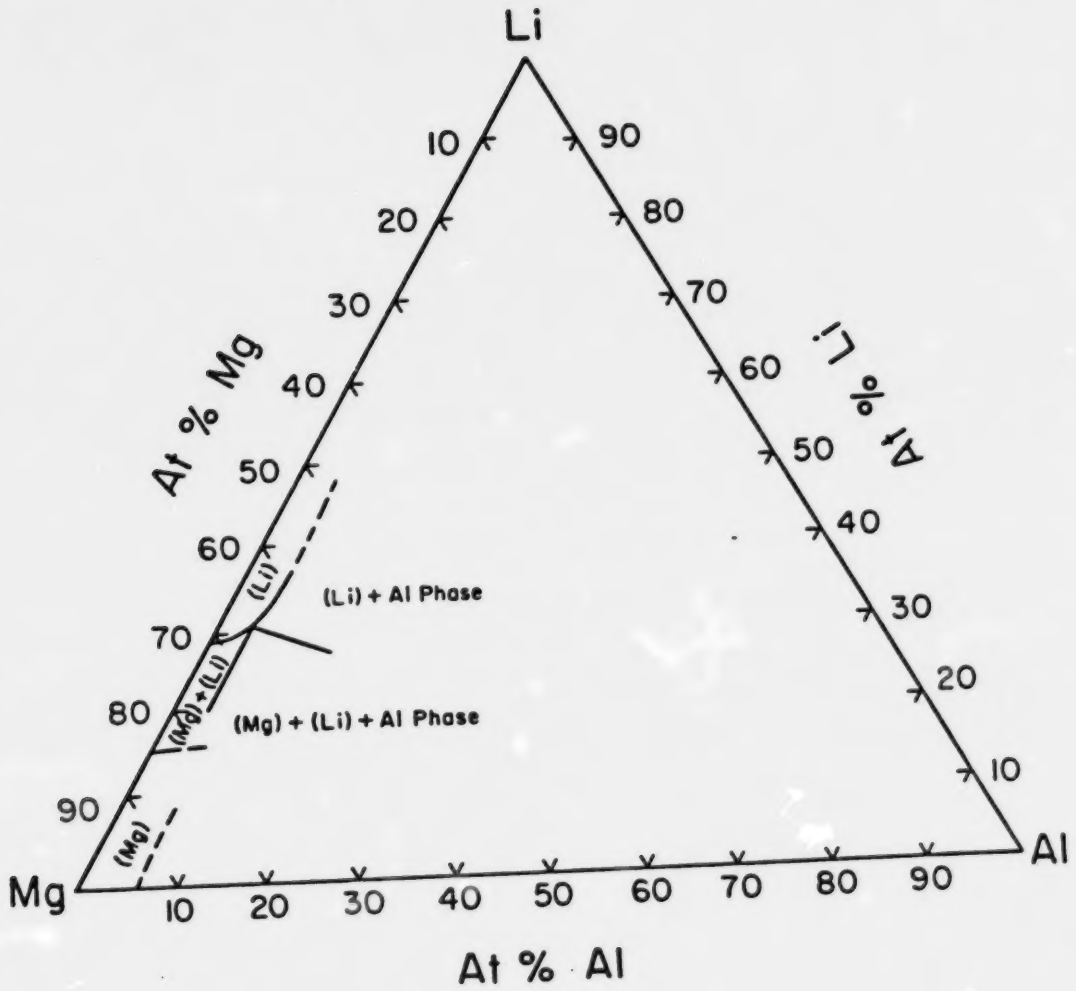
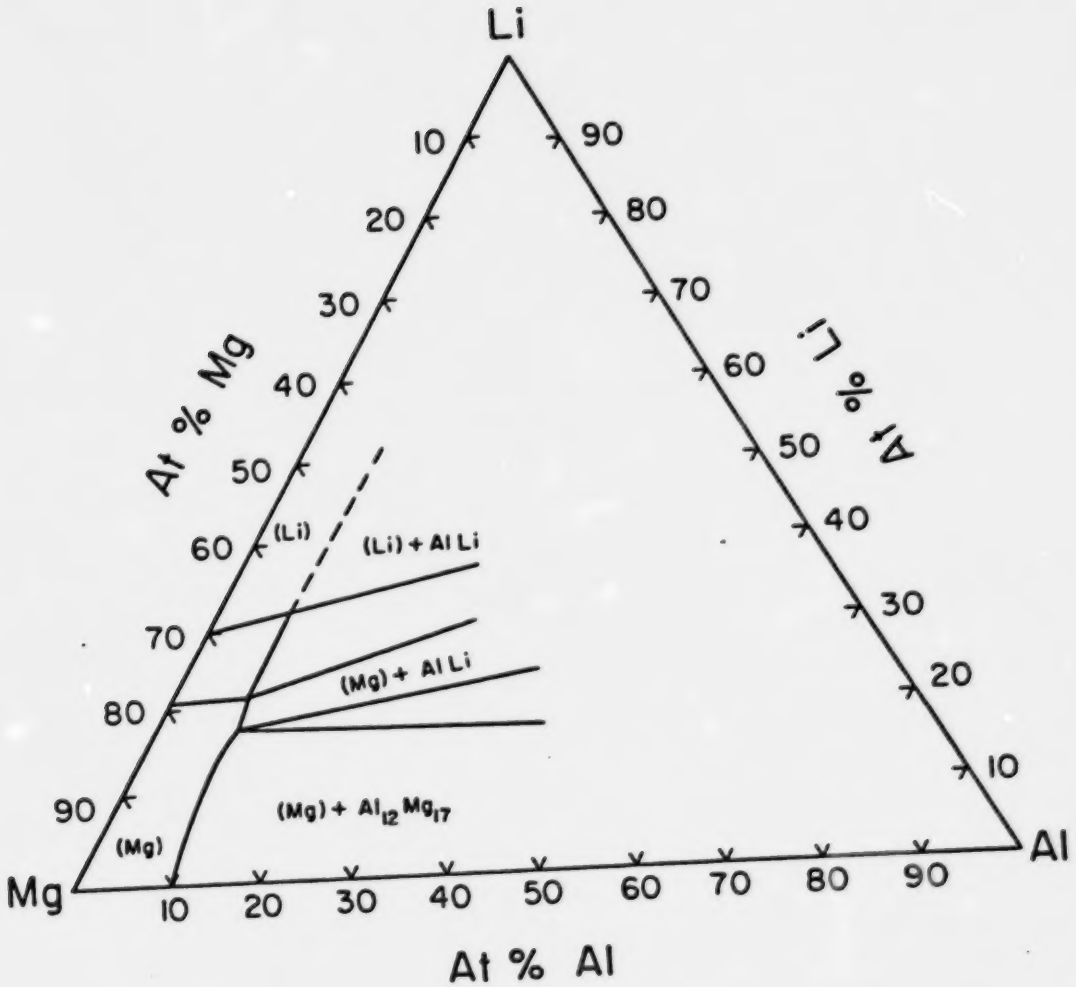

Li
Mg
Al
At % Mg
At % Al
At % Li
10
20
30
40
50
60
70
80
90
(Li) + Al Phase
(Mg) + (Li) + Al Phase
(Mg)+(Li)
(Li)
(Mg)

Fig. 14


Li
Mg
Al
At % Mg
At % Li
At % Al
(Li)
(Li) + Al Li
(Mg) + Al Li
(Mg) + $Al_{12}Mg_{17}$
(Mg)
10
20
30
40
50
60
70
80
90

Ftg. 15

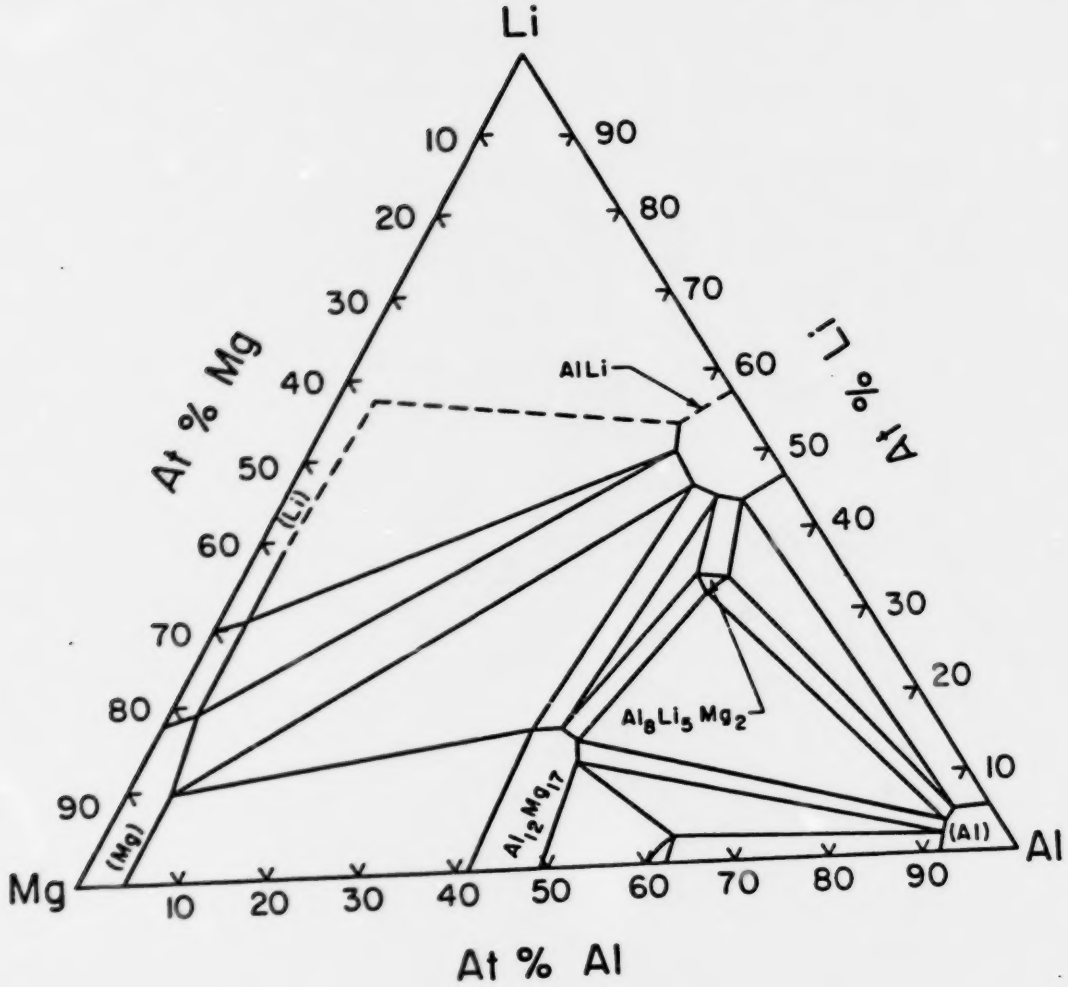

Li
Mg
Al
At % Mg
At % Li
At % Al
AlLi
(Li)
(Mg)
(Al)
$Al_8Li_5Mg_2$
$Al_{12}Mg_{17}$
10
20
30
40
50
60
70
80
90

Fig. 16

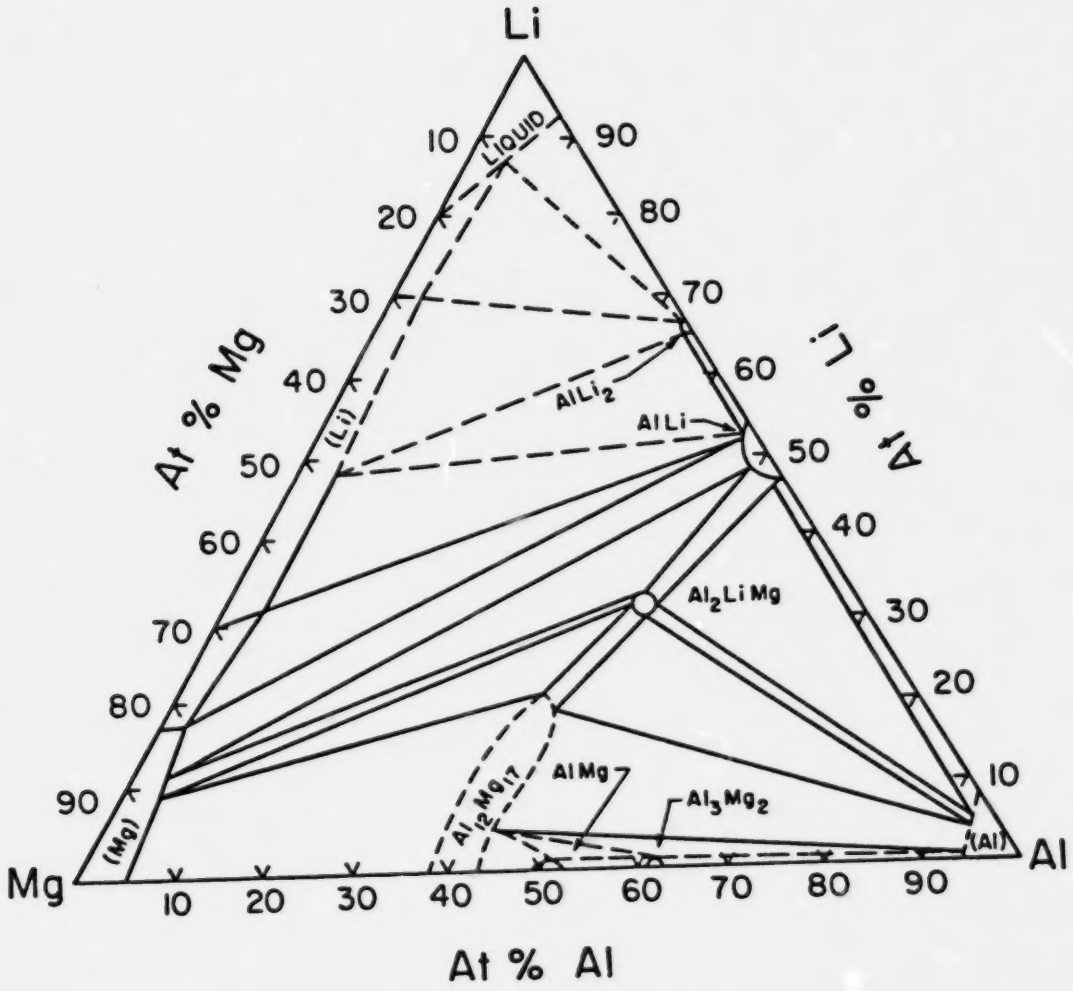

Li
Mg
Al
At % Mg
At % Al
At % Li
10
20
30
40
50
60
70
80
90
Liquid
(Li)
(Mg)
(Al)
AlLi2
AlLi
Al2LiMg
AlMg
Al3Mg2
Al12Mg17

Fig. 17

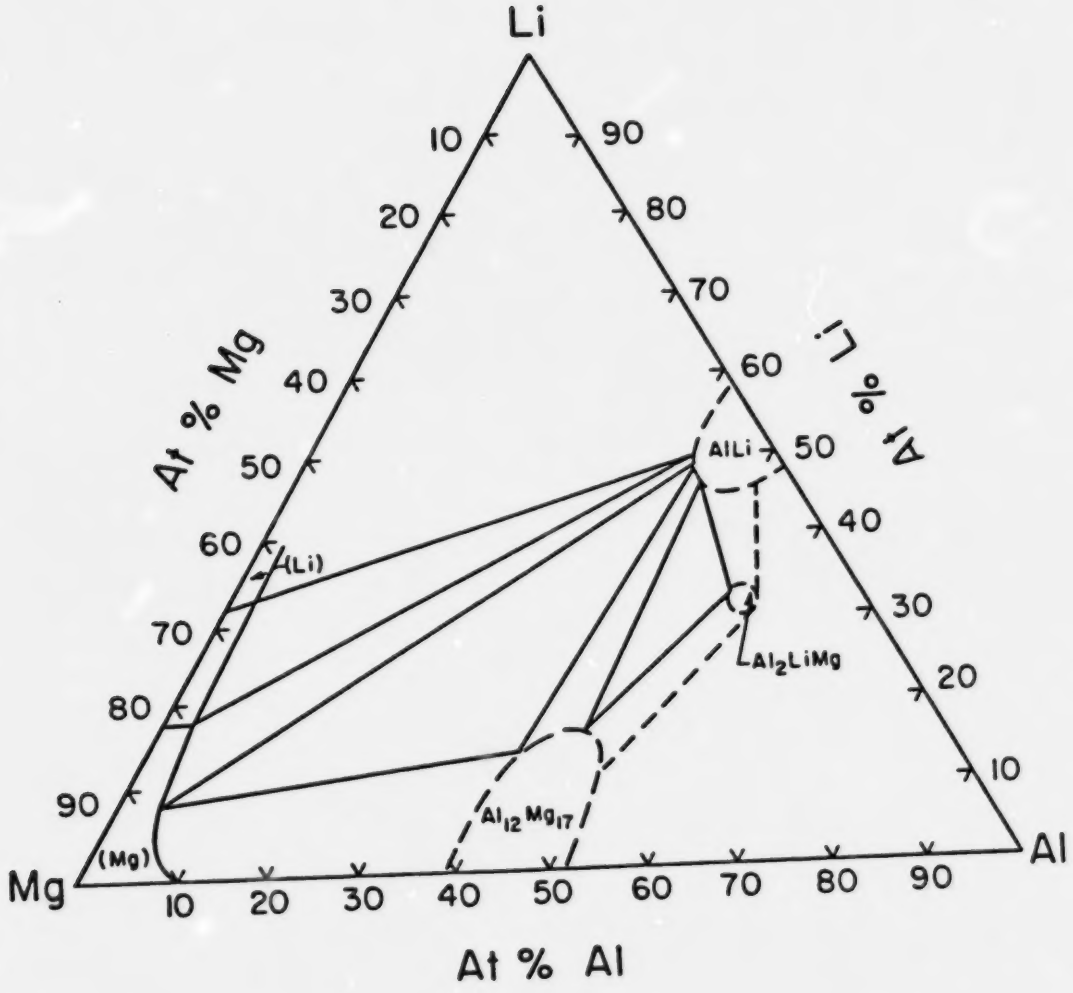

Li
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90
AlLi
(Li)
(Mg)
Al_2LiMg
$Al_{12}Mg_{17}$

Fig. 18

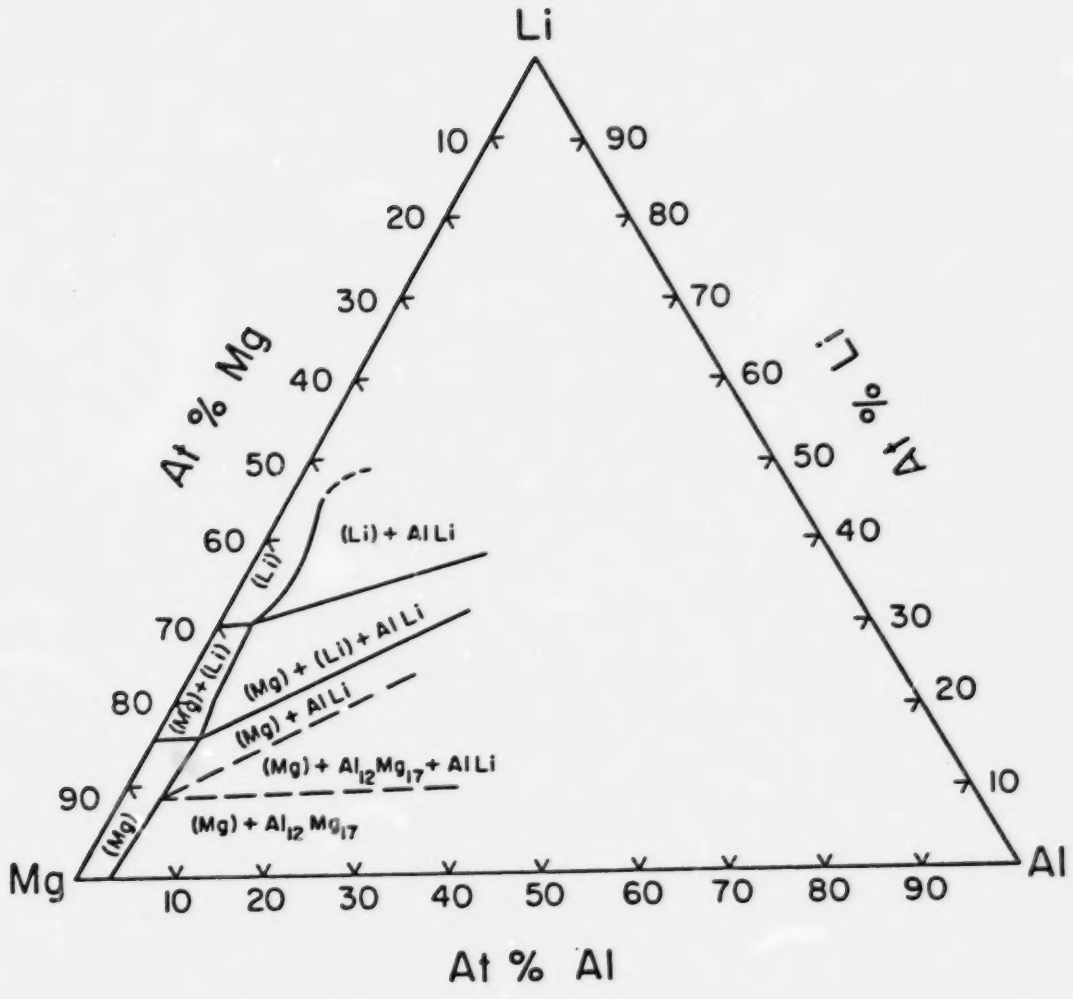

Li
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90
(Li) + Al Li
(Li)
(Mg) + (Li) + Al Li
(Mg) + (Li)
(Mg) + Al Li
(Mg) + Al12Mg17 + Al Li
(Mg) + Al12 Mg17
(Mg)

Fig. 19

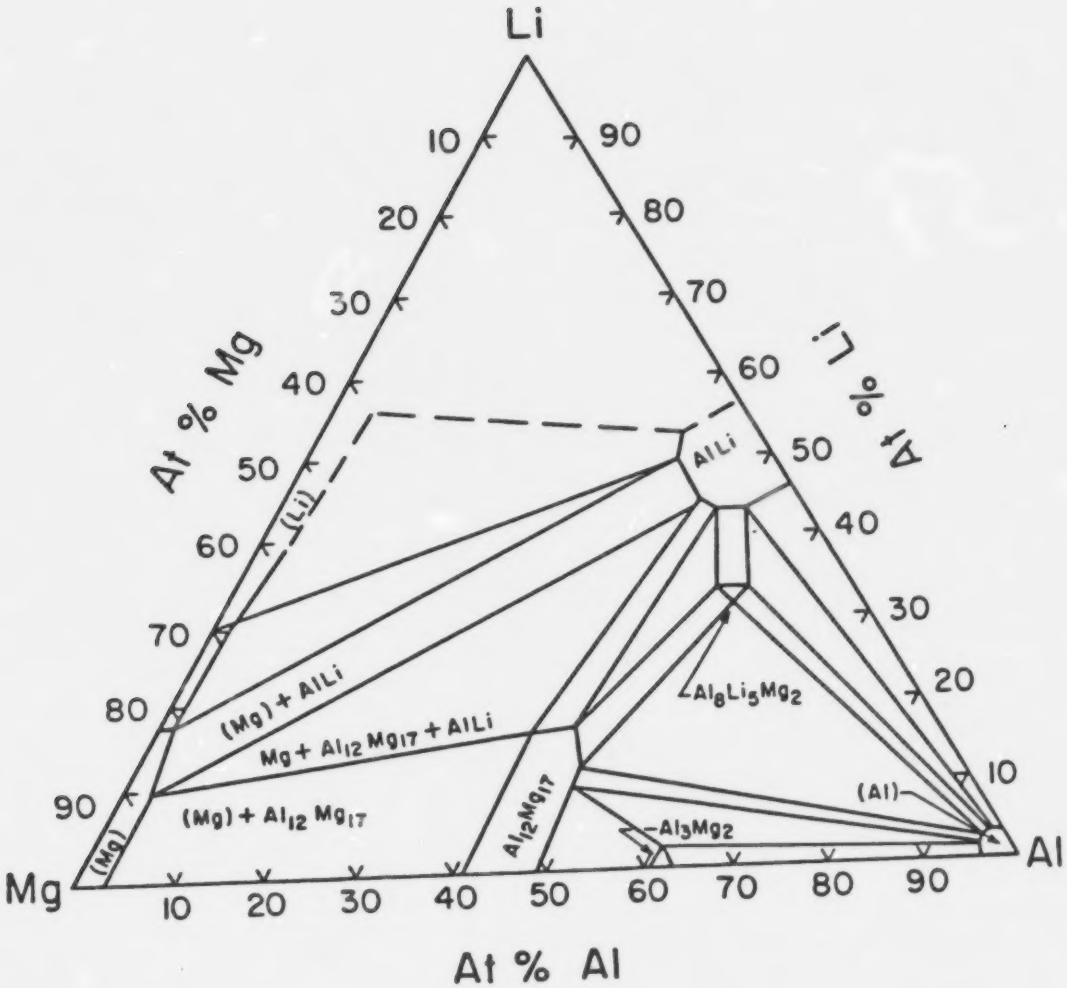

Li
Mg
Al
At % Mg
At % Al
At % Li
10
20
30
40
50
60
70
80
90
(Li)
AlLi
(Mg) + AlLi
Mg + Al12 Mg17 + AlLi
(Mg) + Al12 Mg17
(Mg)
Al12Mg17
Al8Li5Mg2
Al3Mg2
(Al)

Fig. 20

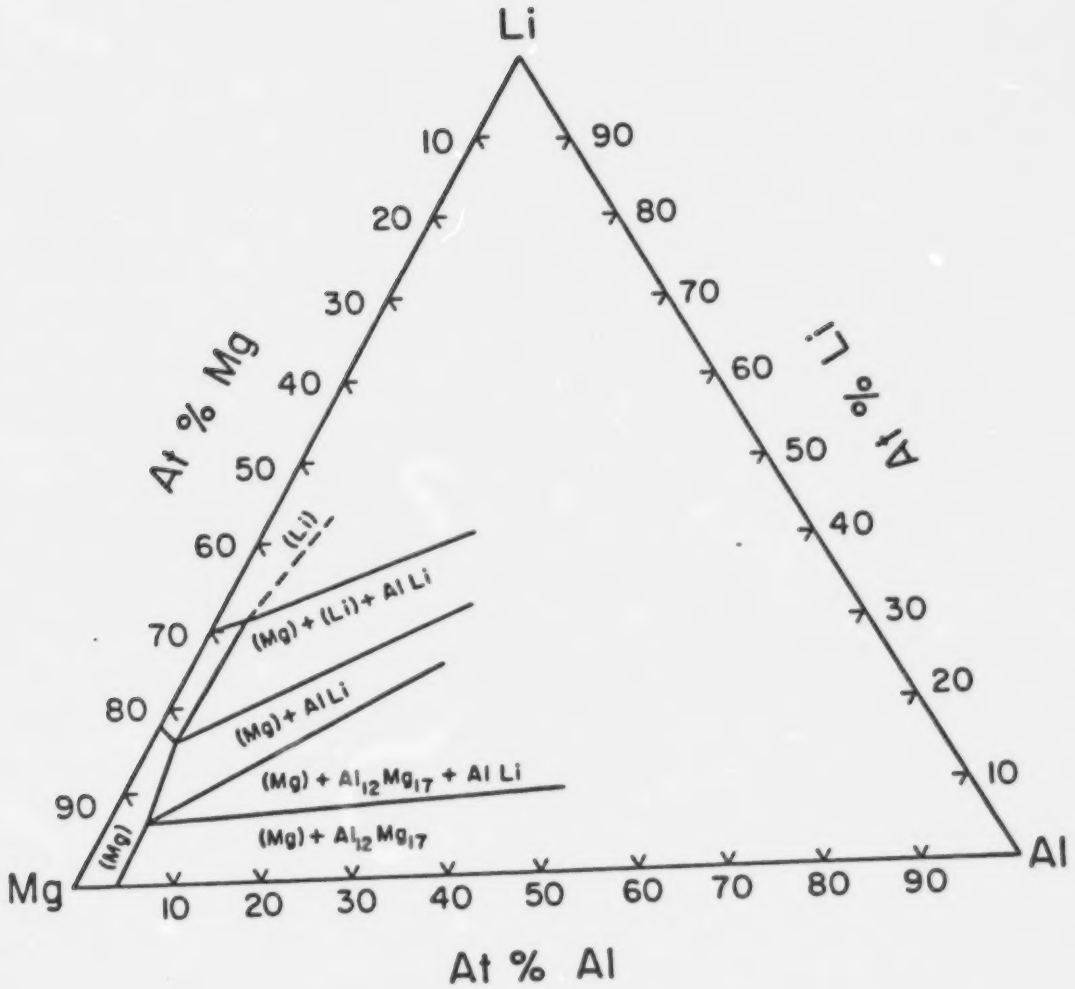

Li
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90
(Li)
(Mg) + (Li) + Al Li
(Mg) + Al Li
(Mg) + Al12Mg17 + Al Li
(Mg) + Al12Mg17
(Mg)

Fig. 21

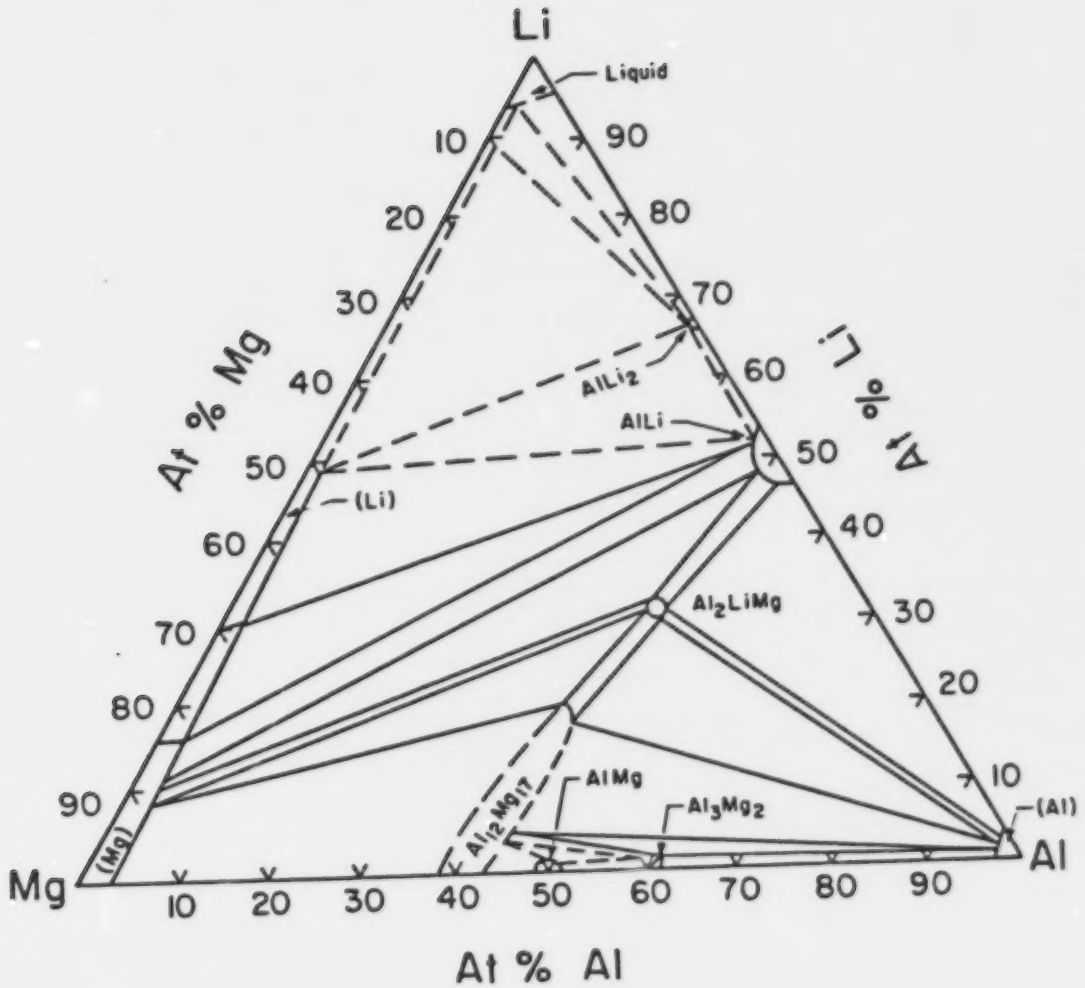

Li
Liquid
10
20
30
40
50
60
70
80
90
At % Mg
AlLi2
AlLi
(Li)
Al2LiMg
AlMg
Al12Mg17
Al3Mg2
(Mg)
(Al)
Mg
Al
10
20
30
40
50
60
70
80
90
At % Al
At % Li

Fig. 22

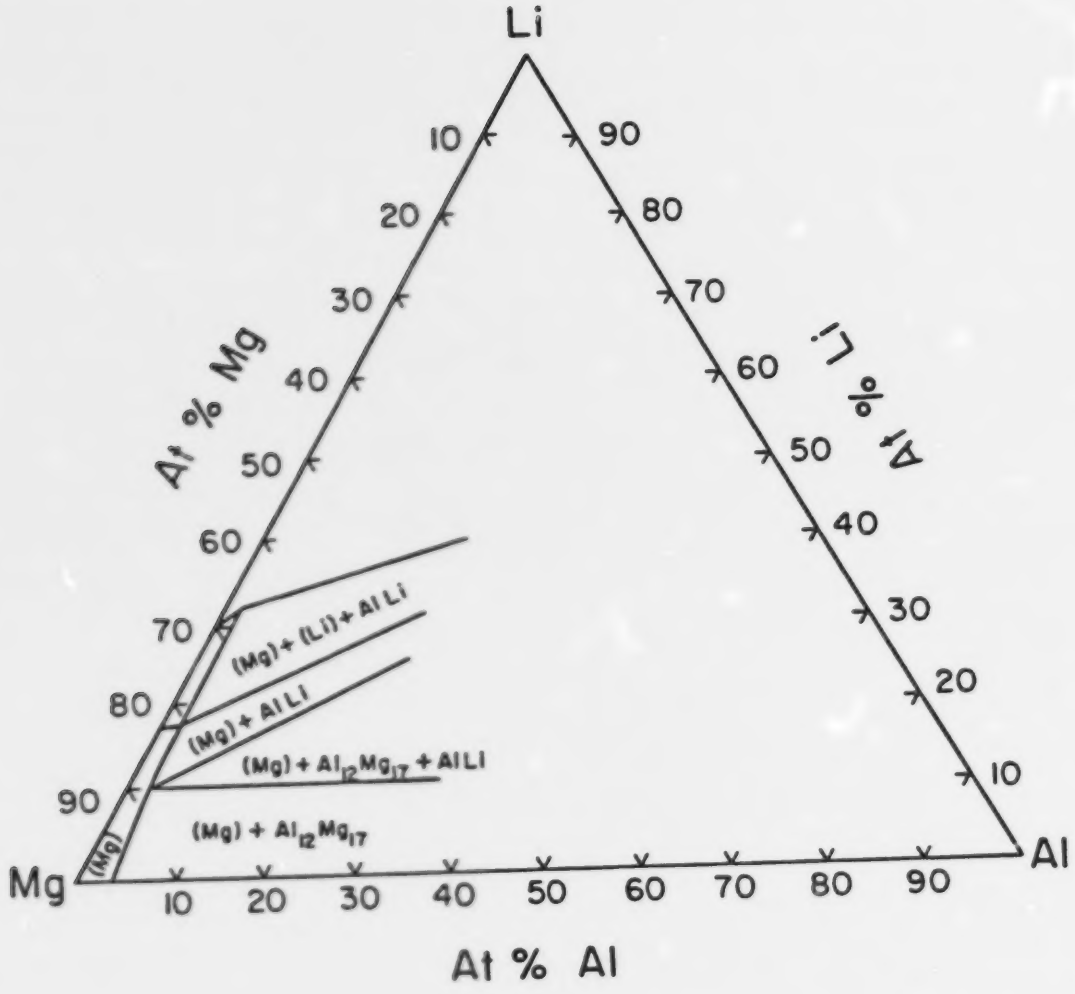

Li
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90
(Mg) + (Li) + Al Li
(Mg) + Al Li
(Mg) + Al12Mg17 + Al Li
(Mg) + Al12Mg17
(Mg)

Fig.23

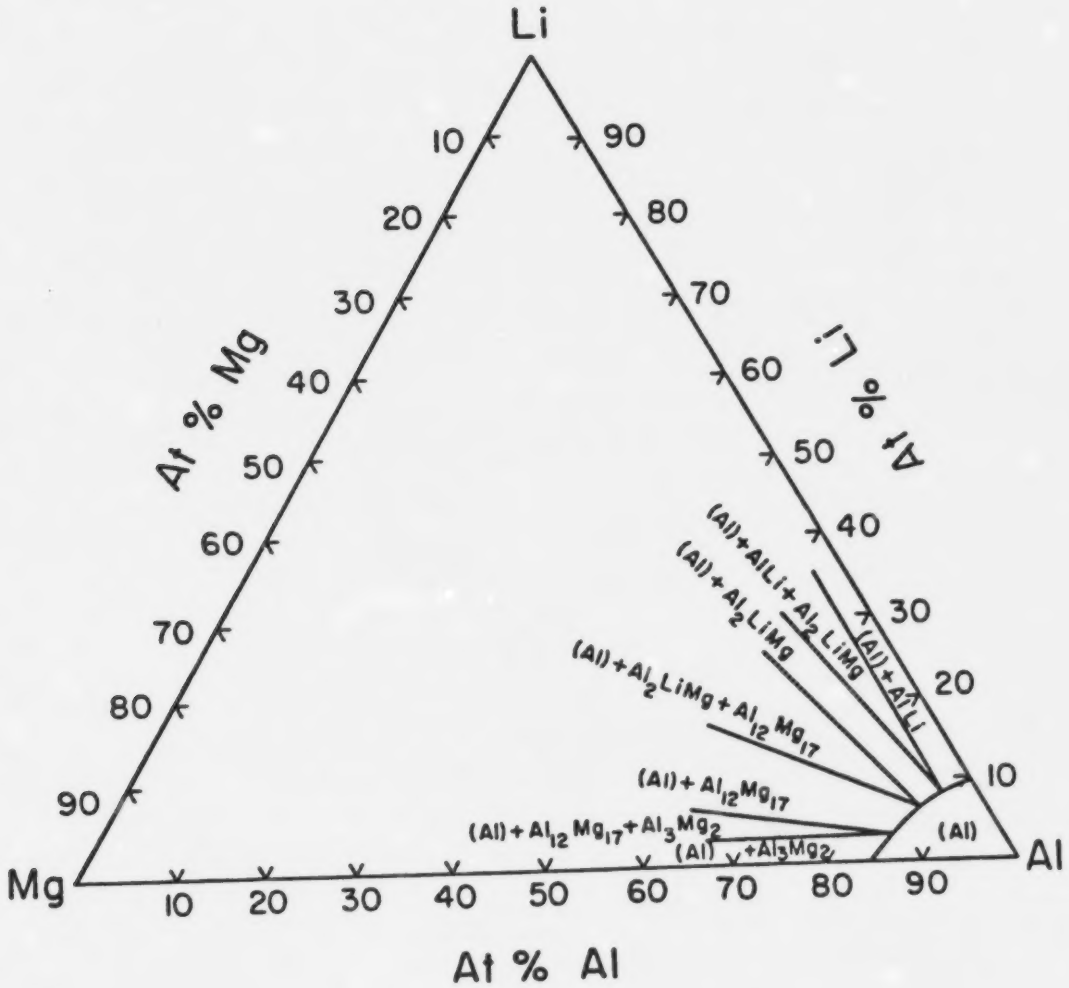
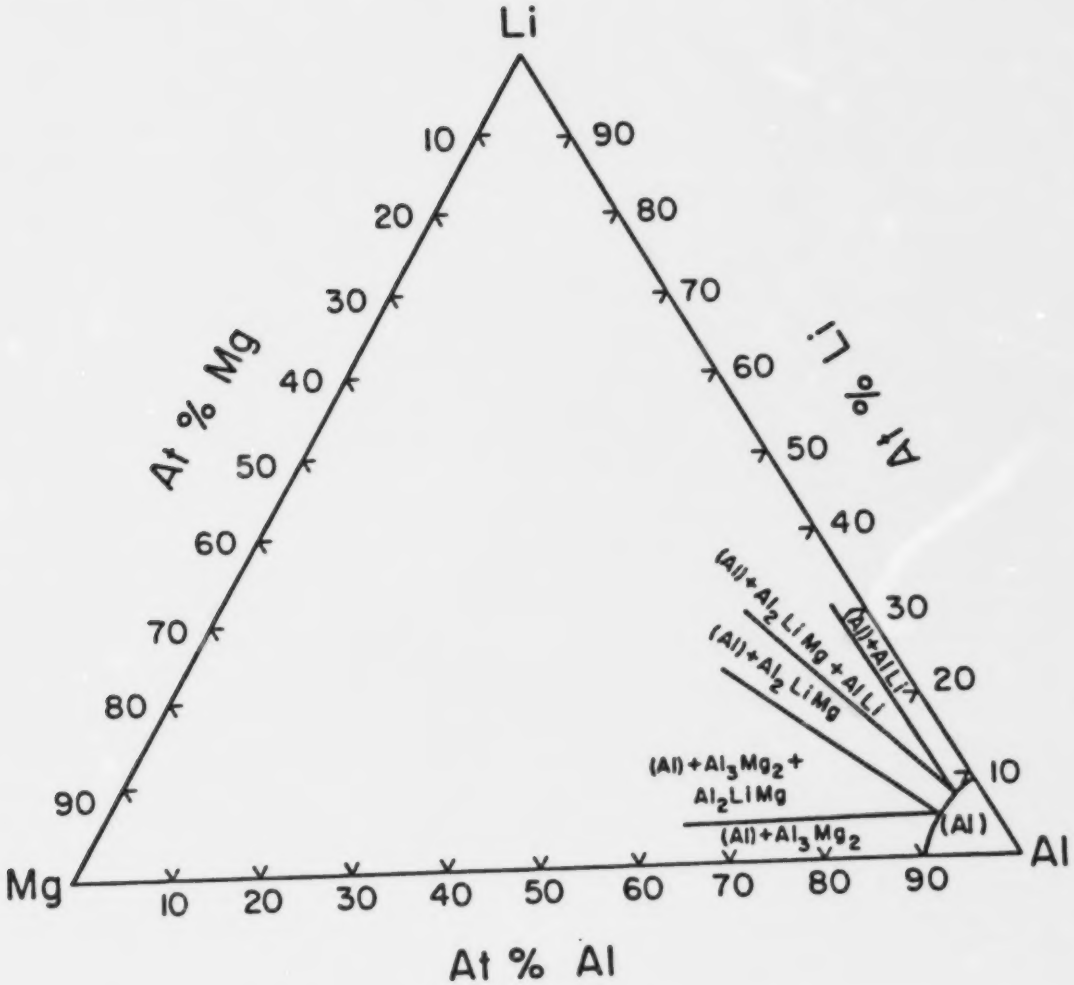

Li
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90
(Al)+AlLi+Al2LiMg
(Al)+Al2LiMg
(Al)+AlLi
(Al)+Al2LiMg+Al12Mg17
(Al)+Al12Mg17
(Al)+Al12Mg17+Al3Mg2
(Al)+Al3Mg2
(Al)

Fig. 24


Li
Mg
Al
At % Mg
At % Li
At % Al
10
20
30
40
50
60
70
80
90
(Al)+Al2LiMg+AlLi
(Al)+Al2LiMg
(Al)+Al3Mg2+
Al2LiMg
(Al)+Al3Mg2
(Al)

Ftg. 25

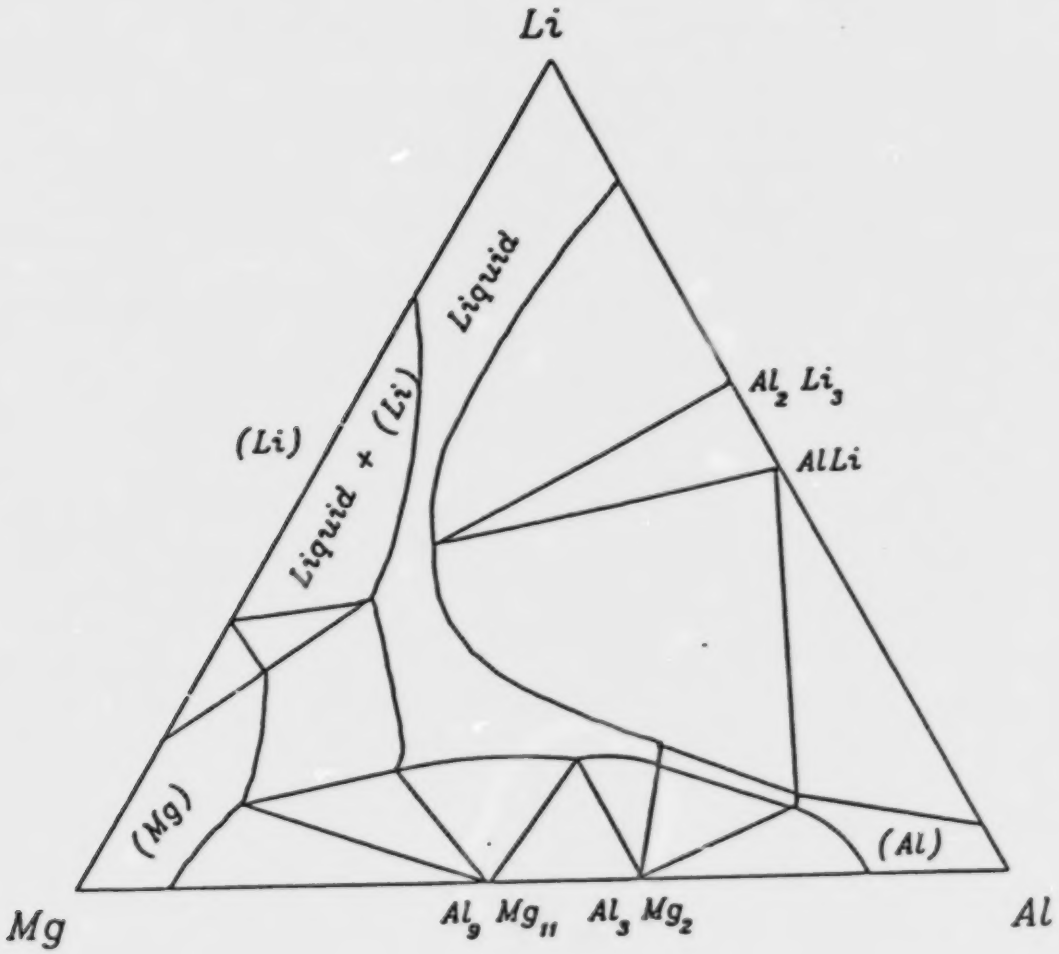


Fig. 26

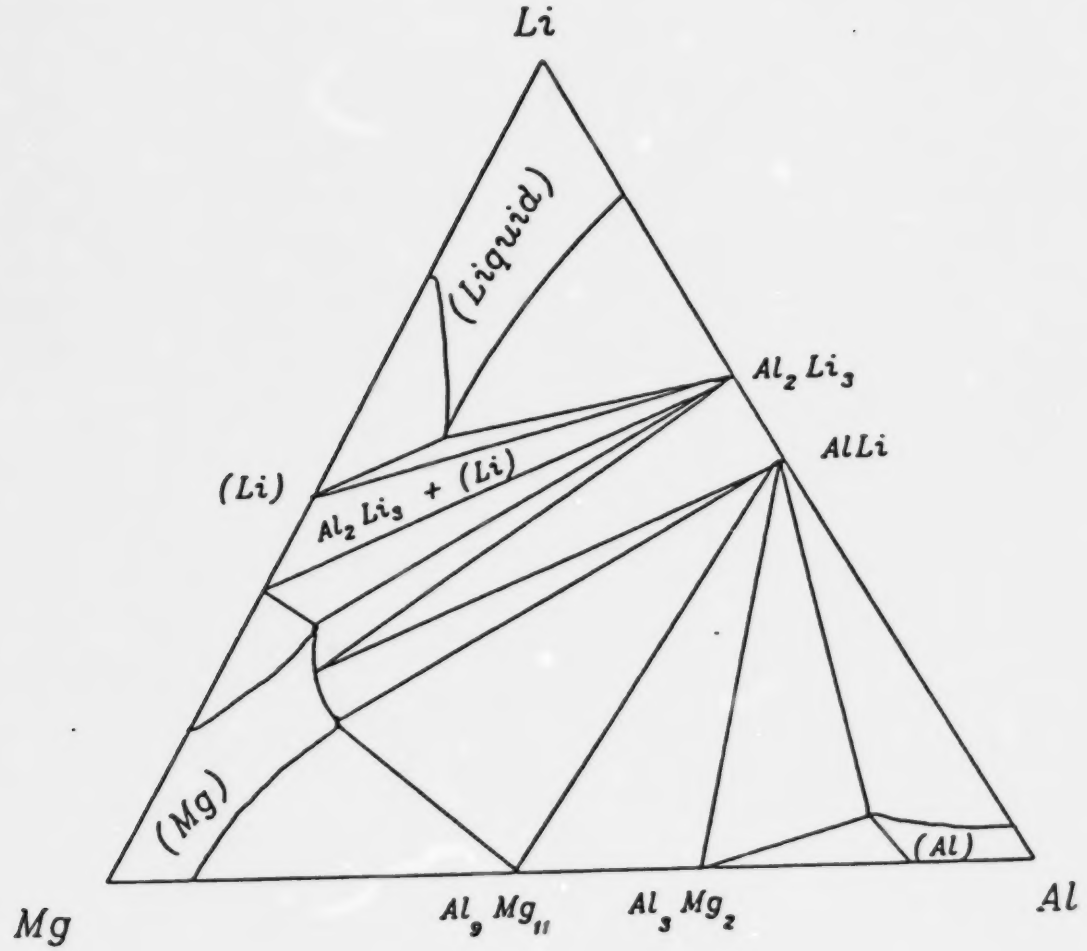


Fig. 27

Aluminum-Lithium-X Ternary Systems

Part II

The Al-Li-Mn (Aluminum-Lithium-Manganese) System

26.98154 6.941 54.9380

The Al-Li-Mn Ternary System

Introduction:

The only studies available to date pertaining to phase equilibria and phase compositions in the Al-Li-Mn system are those due to [63SVI], [67SVI] and [82TAR]. They have studied the system primarily in the Al-rich corner (with 18 w/o and 10 w/o as the maximum Li and Mn contents respectively) employing metallography, X-Ray and thermal analysis in conjunction with hardness determinations. Due to limited solubilities of Li in Mn and vice versa, the Li and Mn rich corner of the system are not expected to be of immediate practical interest and therefore have not been previously studied. Based on the available information on the Al-Li-Mn ternary system, a critical evaluation of this system is made in this note.

Binary Systems:

The binary phase diagrams of Al-Li, Al-Mn and Li-Mn systems are fairly well established [82McA, 65ELL, 65OBI]. Important phases that appear in these binary systems are presented in Table 1, and the important reactions with their corresponding compositions and equilibrium temperatures are summarized in Table 2. At the Al-rich end of Al-Li binary, the occurrence of a eutectic reaction at 869 K (596°C) and a composition of 24.0 a/o (7.5 w/o) lithium is now established with reasonable certainty [82McA] contrary to the eutectic composition of 26 a/o (8.3 w/o) lithium as reported by [37SHA] and 27.75 a/o (9.0 w/o) lithium at 875 K (602°C) as

determined by [67SVI]. [82McA] tabulate a value of 26 a/o Li for the Al-Li eutectic, but all their diagrams show 24 a/o which has been assumed correct in this communication. The present Al-Li-Mn ternary diagrams should therefore be altered to correspond to the most accurate binary diagrams.

The occurrence of a eutectic reaction at ~ 0.95 a/o (1.9 w/o) Mn and 930 K (657°C) as well as a peritectic reaction at 2.05 a/o (4.1 w/o) Mn and 983 K (710°C) at the Al-rich end of Al-Mn binary as reported by [67SVI] agrees with other published information on this system [65ELL]. The Li-Mn binary is characterized by limited solubilities, an immiscibility field in the liquid region, a monotectic reaction at ~ 1526 K (1253°C, 5°C below the melting point of Mn), and an invariant reaction of unknown nature at 453 K (180°C) which is approximately the melting point of Li [650BI]. There are no known compounds in this binary system. The Al-Li, Al-Mn and Li-Mn binary diagrams of [82McA], [65ELL] and [650BI], respectively, have been adopted in the present evaluation of the Al-Li-Mn ternary system.

Pseudobinary Polythermal Sections:

[67SVI] constructed five pseudobinary polythermal sections in deriving the Al-Li-Mn ternary diagram for the Al-rich corner:

1) A polythermal section for Al(2 w/o Li) - Mn (Fig. 1).
2) A polythermal section for a constant Al-content of 92 w/o and varying Li and Mn contents (Fig. 2).
3) Three polythermal sections (Al(Mn)-Li) for constant Mn-contents of 1 w/o, 2.5 w/o and 7 w/o respectively (Figs. 3-5).

A comparison of the points of similar composition from two of their polythermal sections (Figs. 2 and 5) with the Al-Mn binary system shows some inconsistencies which have been appropriately corrected and are shown by dotted curves in these figures. For example, the region of (L + Al_4Mn + Al_6Mn) is replaced by the dotted curves in Figures 2 and 5. A (α + Al_6 Mn + AlLi) region is also shown by a dotted curve in Fig. 1 which was omitted by [67SVI]. Also, for the vertical section at 7% Mn (Figure 5), the phase field at temperatures above 650°C and compositions greater than 9 w/o Li is labeled by [67SVI] as L + AlLi. This is inconsistent with the vertical sections at 1 w/o and 2.5 w/o Mn and we believe that this phase field should be L + Al_4Mn as indicated in parentheses (Fig. 5).

Ternary Diagrams:

The Al-rich corner of the Al-Li-Mn ternary diagram as determined by [67SVI] is reproduced in Fig. 6. The following regions of interest and the important reactions are identified from this figure:

1) Region Al • e_1 • E • e_2 • Al: The region of primary crystallization of the aluminum based (Al)-solid solution.
2) Region e_1 • n_1 • P • E • e_1: The region of primary crystallization of the solid solution based on Al_6Mn.
3) Two phases AlLi and Al_6Mn are in equilibrium with the aluminum solid solution.
4) An invariant ternary eutectic reaction, Liquid $\rightleftharpoons$ (Al) + Al_6Mn + AlLi as determined by x-ray and thermal analysis at a temperature of 870 K (597°C) and a composition of 1.7 w/o (0.67 a/o) Mn, 8.8 w/o (27.47 a/o) Li and 89.5 w/o (71.86 a/o) Al.

5) An invariant ternary peritectic reaction,

Liquid + $Al_4Mn \rightleftharpoons AlLi + Al_6Mn$ also determined by x-ray and thermal analysis at a temperature of 913 K (640°C) and a composition of 3.2 w/o (1.2 a/o) Mn, 9.0 w/o (28.13 a/o) Li and 87.8 w/o (70.61 a/o) Al.

Other than this ternary section, no other detailed liquidus, solidus or isothermal sections are available for this system to confirm the phase compositions and relationships.

Using the modified polythermal sections of [67SVI] as presented earlier and the latest Al-Li binary diagram of [82McA], the liquidus surface and several isothermal sections are presented for the Al-Li-Mn ternary system.

Liquidus Surfaces:

The only portion of the liquidus in the Al-rich region that were experimentally determined by [67SVI] are the ternary eutectic reaction, L → (Al) + Al_6Mn + AlLi, and the ternary peritectic reaction, L + Al_4Mn → AlLi + Al_6Mn, as shown in Fig. 6.

The ternary eutectic reaction occurs at 597°C and a composition of 0.67 a/o Mn, 27.47 a/o Li and 71.86 a/o Al and the ternary peritectic reaction occurs at 640°C and a composition of 1.26 a/o Mn, 28.13 a/o Li and 70.61 a/o Al as determined by [67SVI] using x-ray and thermal analysis. Whereas the ternary eutectic and peritectic compositions of [67SVI] have been assumed to be correct, the ternary eutectic temperature of 597°C is considered inconsistent with the accepted Al-Li binary eutectic at 596°C [82McA] instead of 602°C [67SVI]. The ternary eutectic temperature assumed in this evaluation has therefore been changed from 597°C of

[67SVI] to 591°C to agree with the current Al-Li binary. Fig. 7 shows the liquidus surfaces at various tempertures as derived from the polythermal sections (Figs. 1-5) and the binary diagrams.

Isothermal Sections:

Representative isothermal sections at 550°C, 593°C, 610°C, 645°C and 655°C have been constructed from the modified polythermal sections (Figs. 1-5) and are shown in Figs. 8-12.

Regions of Primary Crystallization and Ternary Compounds:

Regions of primary crystallization in the Al-rich end of this system are:

a) Al-base α-solid solution

b) Solid solution based on Al_6Mn

c) Solid solution based on Al_4Mn

d) Solid solution based on AlLi

There are no ternary compounds reported at the Al-rich end of this system. [68DRI] and [63SVI] reported that Mn and Li have very limited solubilities in the compounds AlLi and Al_6Mn respectively. However, [71KAD] have speculated that Al_6Mn can dissolve up to about (5.5 w/o) lithium. [82TAR] have reported the presence of the phase Al_3Li in addition to AlLi and Al_6Mn in hardened and aged 1.5 w/o Mn, 2.9 w/o Li 95.6 w/o Al alloy. Al_3Li is a metastable ordered phase and has been detected and delineated in the Al-Li binary by [80WIL]. It has been shown to precipitate only at temperatures below 673 K (400°C), which is below

the experimental temperature of [67SVI] and has therefore been missed in their investigations.

Conclusions:

From the limited experimental work of [67SVI], the conclusions that can be drawn regarding the phase equilibria and phase compositions in the Al-Li-Mn ternary system are:

1) At the Al-rich corner no ternary phase is formed and the fields of primary crystallization are Al, AlLi, Al_6Mn and Al_4Mn.
2) AlLi and Al_6Mn are in equilibrium with the Al-base solid solution containing Li and Mn.
3) Two ternary invariant reactions, a eutectic and a peritectic, are present.
4) Mn and Li have very limited solubilities in the compounds AlLi and Al_6Mn, respectively.
5) Considerable additional work is required to confirm the phase equilibria and phase compositions in the Al-Li-Mn ternary system, particularly at compositions other than the Al-rich corner.

References:

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[65OBI]: Obinata, 1., Takeuchi, Y., Kurihara, K. and Watanabe, M., "Ueber Die Legierungen des Mangans und Siliziums mit Alkali-und Erdalkali-Metallen", Metall., 19(1), pp. 21-35 (1965), in German.

[65ELL]: Elliot, R.P., Constitution of Binary Alloys, First Supplement, pp. 43-45 (1965).

[67SVI]: Sviderskaya, Z.A., Kadaner, E.S. and Turkina, N.I., "Phase Diagram of the Aluminum-Rich Corner of the Al-Mn-Li System", Russian Metallurgy, 2, pp. 103-106 (1967).

[68DRI]: Drits, M.E., Kadaner, E.S. and Turkina, N.I., "A Study of the Phase Diagram of Aluminum Base Alloys", Izv. Akad. Nauka SSSR, pp. 106-118 (1968), in Russian.

[71KAD]: Kadaner, E.S. and Turkina, N.I., "Mechanical Properties and Heat Resistance of the Individual Phases of Alloys of the Al-Mn-Li System", In: Structure and Properties of Light Alloys, Izv. Akad. Nauka SSSR, p. 95 (1971) in Russian.

[80WIL]: Williams, D.B., "Microstructural Characteristics of Al-Li Alloys", In: Aluminum Lithium Alloys, Stone Mountain, Ga., pp. 89-100 (1980).

[82McA]: McAlister, A.J., "The Al-Li (Aluminum-Lithium) System", Bulletin of Alloy Phase Diagrams, 3(2), pp. 177-183 (1982).

[82TAR]: Tarasenko, L.V., Turkina, N.I. and Matveyeva, G.N., "Phase Composition of Aluminum Alloys Al-Mn-Li", Russian Metallurgy, pp. 185-189 (1982).

TABLE 1: Phases and their crystal structure in Al-Li-Mn Ternary System and its Constituent Binaries.

Phase/(Temp.°C)	Symbols used in literature/Ref.	Approximate Composition (at/o)	Pearson Symbol or Crystallographic Structure/Space Group	Prototype	Lattice Parameters in nm a	b	c	Comments
Al-Li Binary System								
Al-Solid Solution < 660.5°C	α[82McA]	0-15 Li	cF4/ Fm3m	Cu	0.40495*	-	-	*At 0 at/o Li
Al Li < 700°C	β[82McA]	45-55 Li	cF16/ Fd3̄m	NaTl	0.637**	-	-	**At 50 a/o Li
Al_2Li_3 < 520°C	γ[82McA]	60-61 Li	hR15/ R3̄m	-	0.4508	-	1.426	
Al_4Li_9 < 275°C	δ[82McA]	Line Compound at 69.2 Li	mC2 6/ C2/m	-	1.91551	0.54288	0.44988	β = 107.67
Al_4Li_9 (275-330°C)	δ'[82McA]	69.2 Li	unclassified	-	-	-	-	
Li-Solid[a] Solution < 180.6°C	(Li)[82McA]	100.0 Li	C I2/ IM 3m	W	-	-	-	
Al_2Li Metastable	α'[82McA]	-	CP4/ Pm3m	-	-	-	-	

TABLE 1: (Continued)

Phase/(Temp.°C)	Symbols used in literature/Ref.	Approximate Composition (at/o)	Pearson Symbol or Crystallographic Structure/Space Group	Prototype	Lattice Parameters in nm a	b	c	Comments
Li-Mn Binary System								
No compounds are found in this system [65OBI]								
Al-Mn-Binary System								
Al-Solid Solution	α	0-0.9 Mn	cF4/ Fm3m	Cu	0.40495	-	-	At 0 at/o Mn
Al_6Mn < 710°C	β[60TAY]	14.2 Mn	orthorhombic/ Cmcm		0.65	0.755	0.887	
Al_4Mn or < 822	γ[60TAY]	17.4-19.5	Hexagonal	-	2.84	-	1.24	

Note: Higher Mn phases are not listed here and are assumed to be the same as listed by [65ELL]

Al-Li-Mn Ternary System

Note: No ternary compounds/phases are known to exist.

Table 2

Reaction Symbol	Reactions
Al-Li System [82McA] (compositions in a/o Li)	
e_1	$L(24\ a/o) \underset{}{\overset{600°C}{\rightleftharpoons}} \alpha^*(14\ a/o) + \beta^*(45\ a/o)$
P_1	$\beta(55\ a/o) + L(77\ a/o) \overset{520°C}{\rightleftharpoons} \gamma^*(60\ a/o)$
P_2	$L(90\ a/o) + \gamma^*(60\ a/o) \overset{335°C}{\rightleftharpoons} \delta^{*\prime}(69\ a/o)$
?	$\gamma(60\ a/o)\ \delta/\delta'(69\ a/o)\ L(95\ a/o)$ at 275°C
e_2	$L(98\ a/o) \overset{177°C}{\rightleftharpoons} \delta(69\ a/o) + \text{bcc Li}(100\ a/o)$
Al-Mn System [65ELL] (Composition in a/o Mn)	
e_1	$L(0.95\ a/o) \overset{657°C}{\rightleftharpoons} (Al)\ (0.9\ a/o) + Al_6Mn(14.2\ a/o)$
P_1	$L(2.06\ a/o) + Al_6Mn\ (17.4\ a/o) \overset{710°C}{\rightleftharpoons} Al_6Mn\ (14.2\ a/o)$

*α = (Al), β = Al Li, γ = Al_2Li_3, δ/δ' = Al_4Li_9.

Figure Captions:

Fig. 1. Polythermal section of the Al-Li-Mn Diagram for constant content of 2 w/o Li.

Fig. 2. Polythermal section for constant content of 92 w/o Al.

Fig. 3. Polythermal section for constant content of 1 w/o Mn.

Fig. 4. Polythermal section for constant content of 2.5 w/o Mn.

Fig. 5. Polythermal section for constant content of 7 w/o Mn.

Fig. 6. Al-rich corner of the Al-Li-Mn Ternary Diagram after [67SVI].

Fig. 7. Speculative liquidus for the Al-rich corner of the Al-Li-Mn system.

Fig. 8. Isothermal section at 550°C.

Fig. 9. Isothermal section at 593°C.

Fig. 9a. Expanded portion of Fig. 9.

Fig. 10. Isothermal section at 610°C.

Fig. 11. Isothermal section at 645°C.

Fig. 12. Isothermal section at 655°C.

Fig. 1

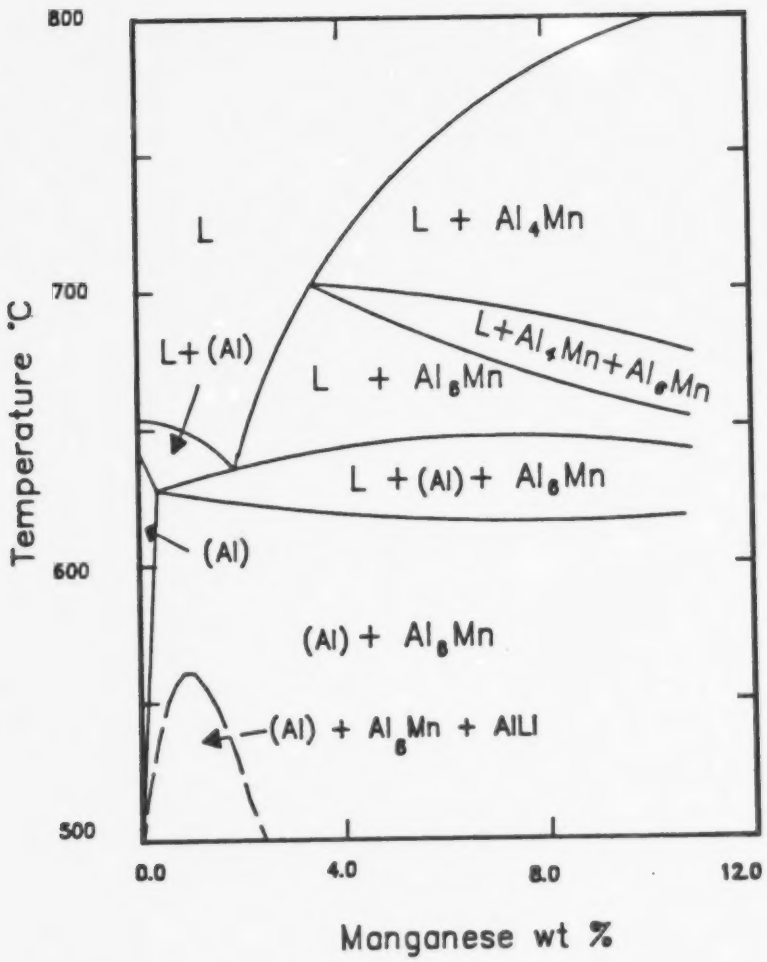

800
700
600
500
Temperature °C
L
L + Al4Mn
L+(Al)
L + Al6Mn
L+Al4Mn+Al6Mn
L + (Al) + Al6Mn
(Al)
(Al) + Al6Mn
(Al) + Al6Mn + AlLi
0.0
4.0
8.0
12.0
Manganese wt %

Fig. 2

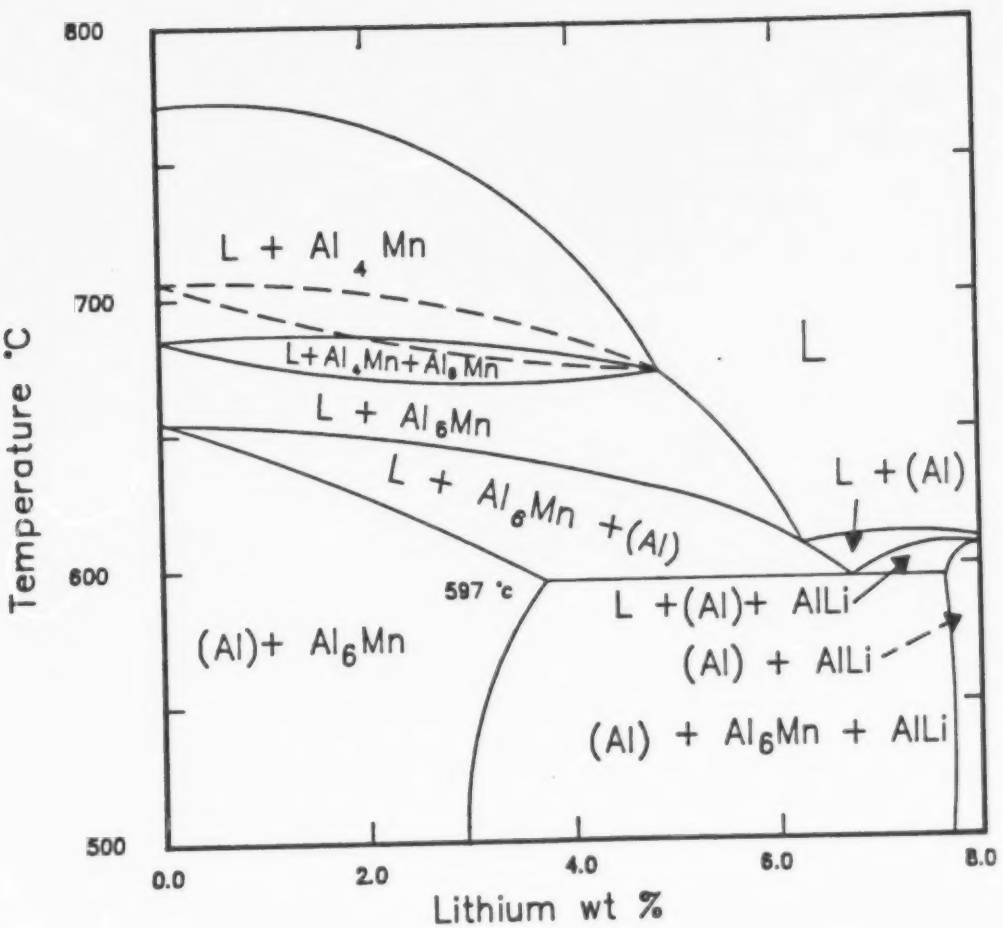

800
700
600
500
Temperature °C
L + Al4Mn
L
L+Al4Mn+Al6Mn
L + Al6Mn
L + Al6Mn +(Al)
L +(Al)
597 °c
L +(Al)+ AlLi
(Al)+ Al6Mn
(Al) + AlLi
(Al) + Al6Mn + AlLi
0.0
2.0
4.0
6.0
8.0
Lithium wt %

Fig. 3

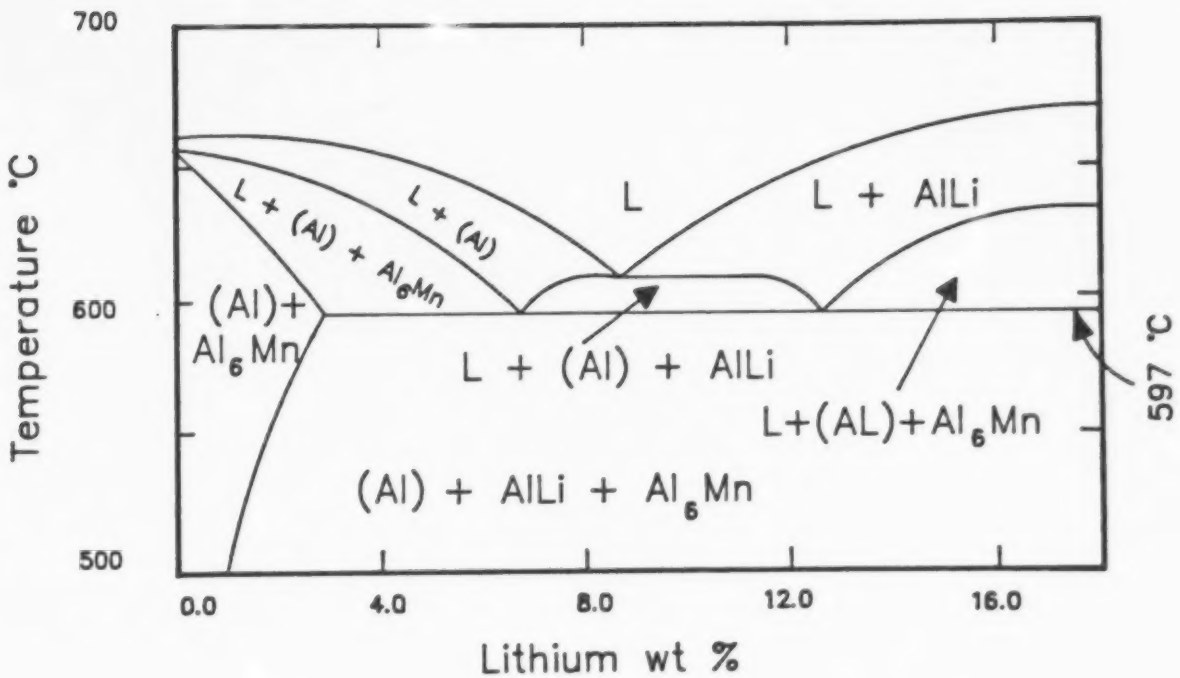

700
600
500
Temperature °C
L + (Al) + Al6Mn
L + (Al)
L
L + AlLi
(Al)+
Al6Mn
L + (Al) + AlLi
L+(AL)+Al6Mn
597 °C
(Al) + AlLi + Al6Mn
0.0
4.0
8.0
12.0
16.0
Lithium wt %

Fig. 4

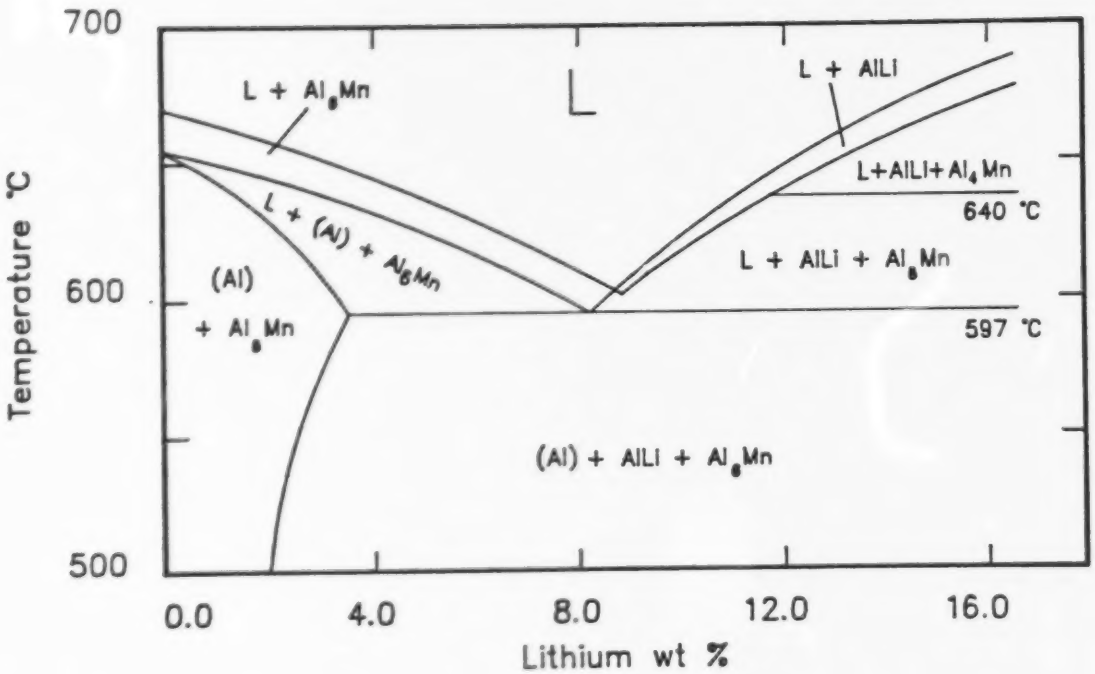

700
600
500
Temperature °C
L + Al6Mn
L
L + AlLi
L+AlLi+Al4Mn
640 °C
L + (Al) + Al6Mn
L + AlLi + Al6Mn
(Al)
+ Al6Mn
597 °C
(Al) + AlLi + Al6Mn
0.0
4.0
8.0
12.0
16.0
Lithium wt %

Fig. 5

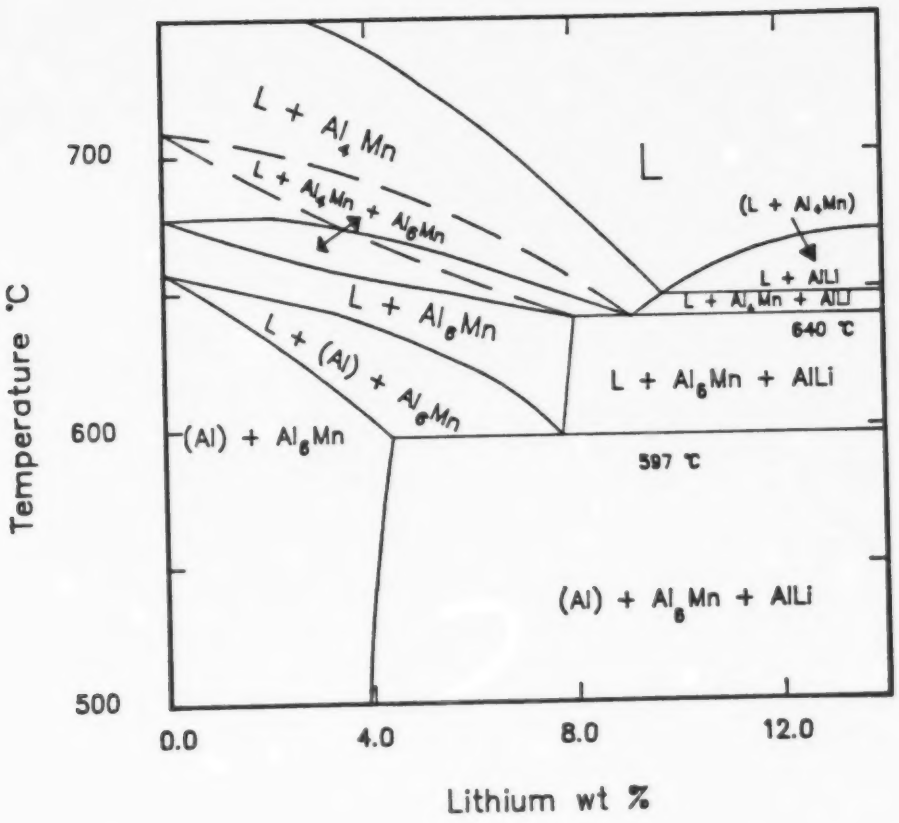

L + Al_4Mn
L
L + Al_4Mn + Al_6Mn
(L + Al_4Mn)
L + AlLi
L + Al_4Mn + AlLi
640 ℃
L + Al_6Mn
L + (Al) + Al_6Mn
L + Al_6Mn + AlLi
(Al) + Al_6Mn
597 ℃
(Al) + Al_6Mn + AlLi
700
600
500
0.0
4.0
8.0
12.0
Temperature °C
Lithium wt %

Fig. 6

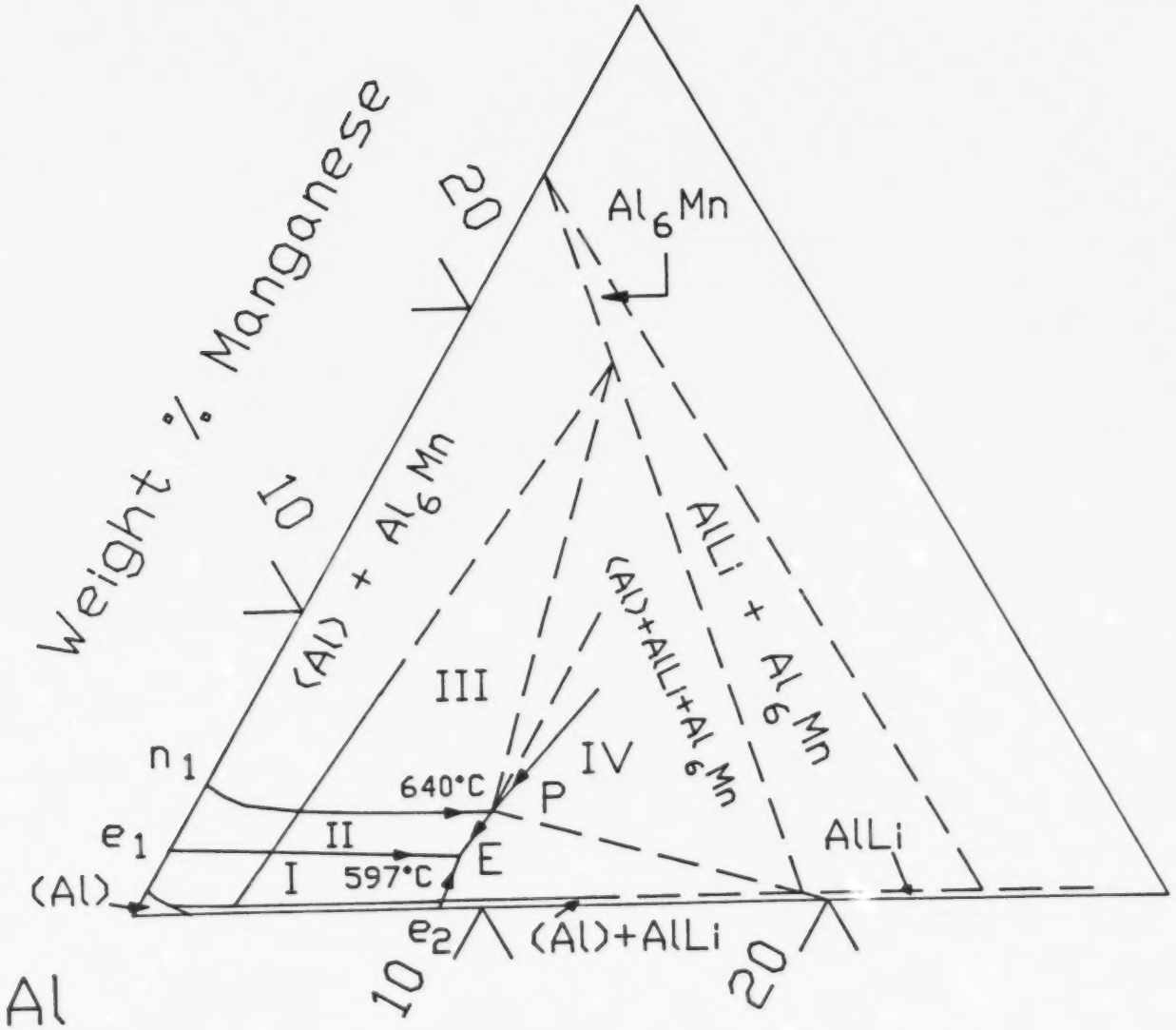

Weight % Manganese
20
10
Al6Mn
(Al) + Al6Mn
AlLi + Al6Mn
(Al)+AlLi+Al6Mn
III
IV
n1
640°C
P
e1
II
E
I
597°C
(Al)
AlLi
e2
(Al)+AlLi
Al
10
20
Weight % Lithium

Fig. 7

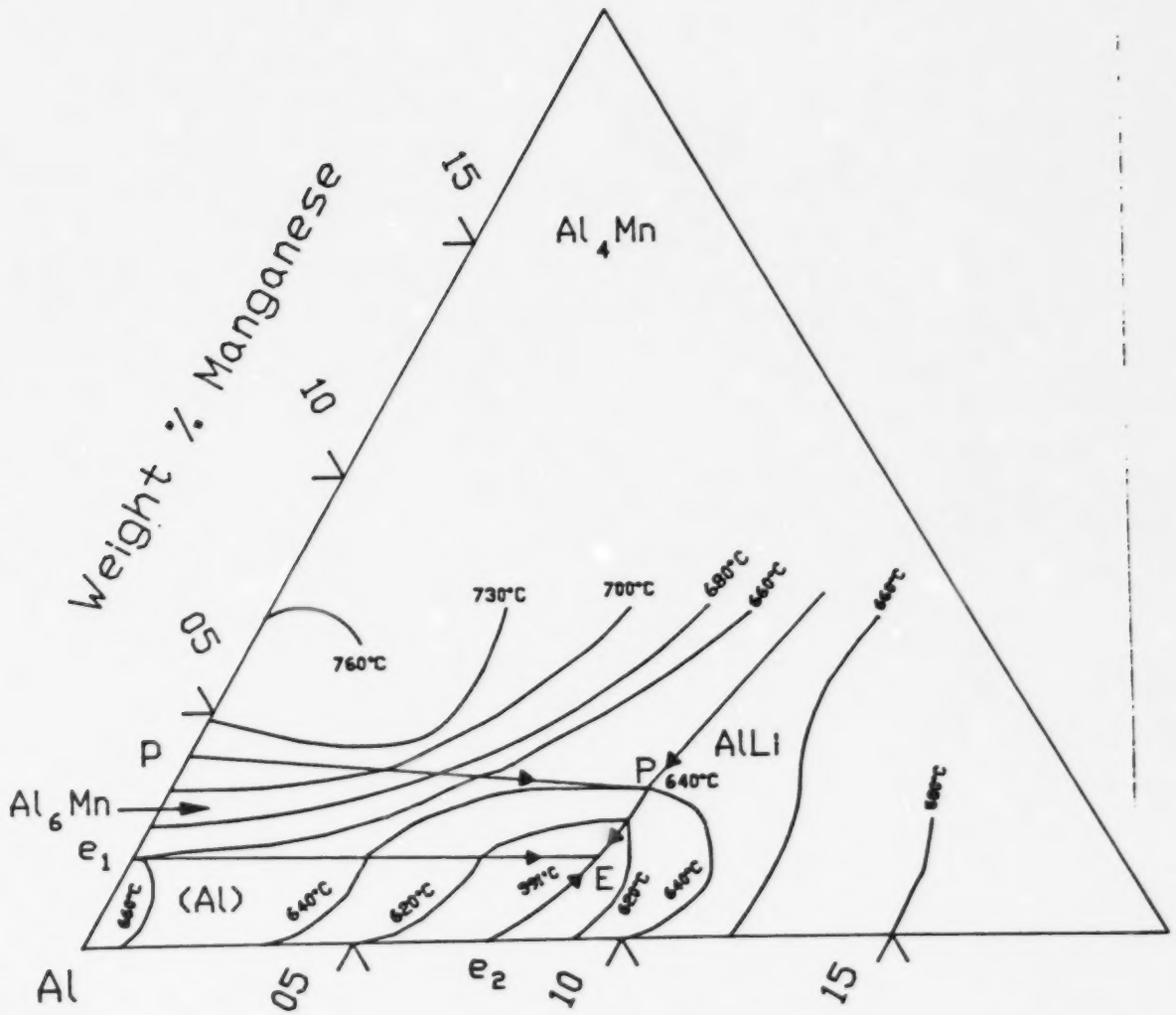

Weight % Manganese
05
10
15
Al4Mn
760°C
730°C
700°C
680°C
660°C
640°C
P
P
AlLi
Al6Mn
e1
(Al)
640°C
620°C
591°C
E
625°C
640°C
Al
05
e2
10
15
Weight % Lithium

Fig. 8

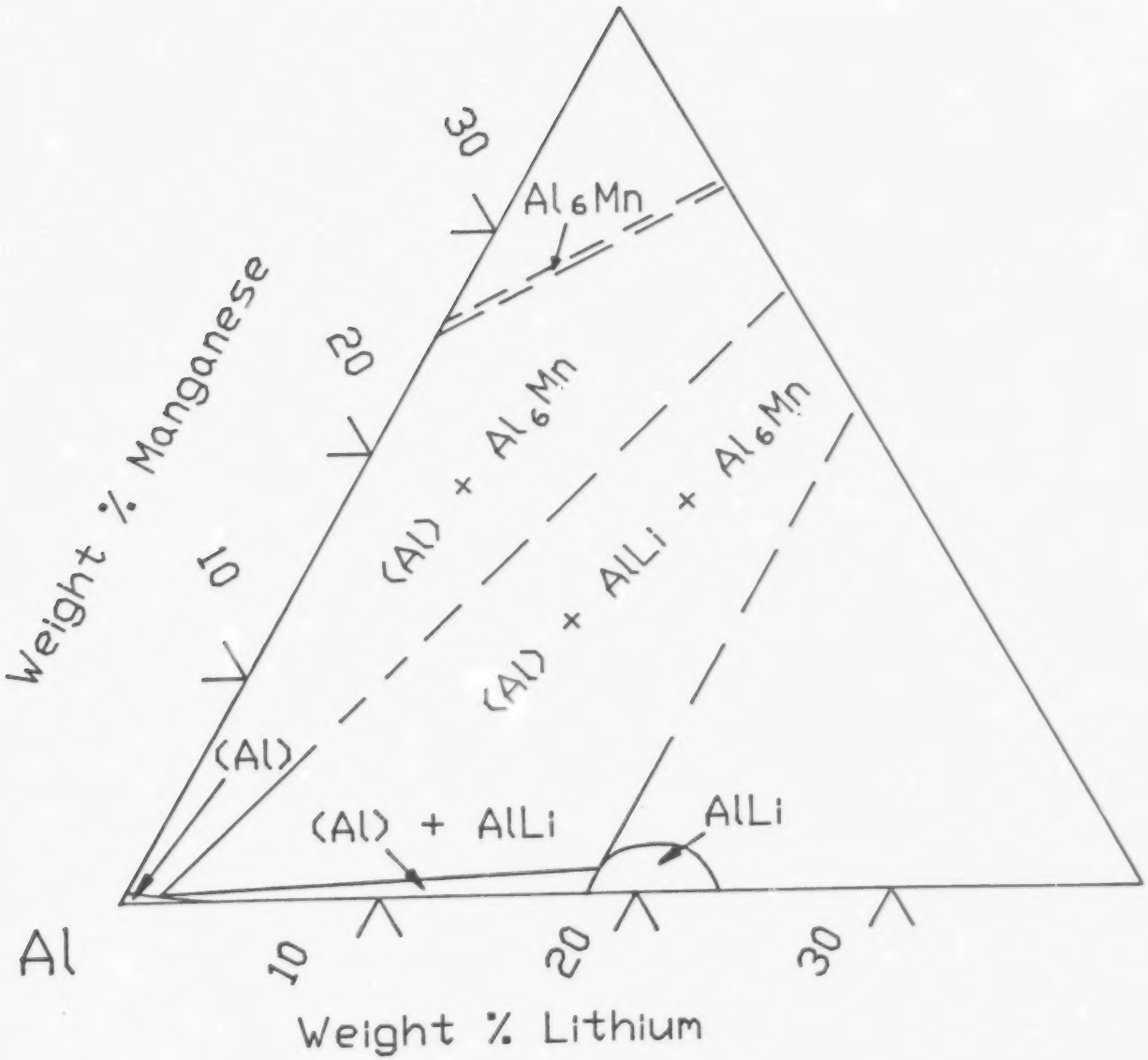

Weight % Manganese
30
20
10
Al6Mn
(Al) + Al6Mn
(Al) + AlLi + Al6Mn
(Al)
(Al) + AlLi
AlLi
Al
10
20
30
Weight % Lithium

Fig. 9

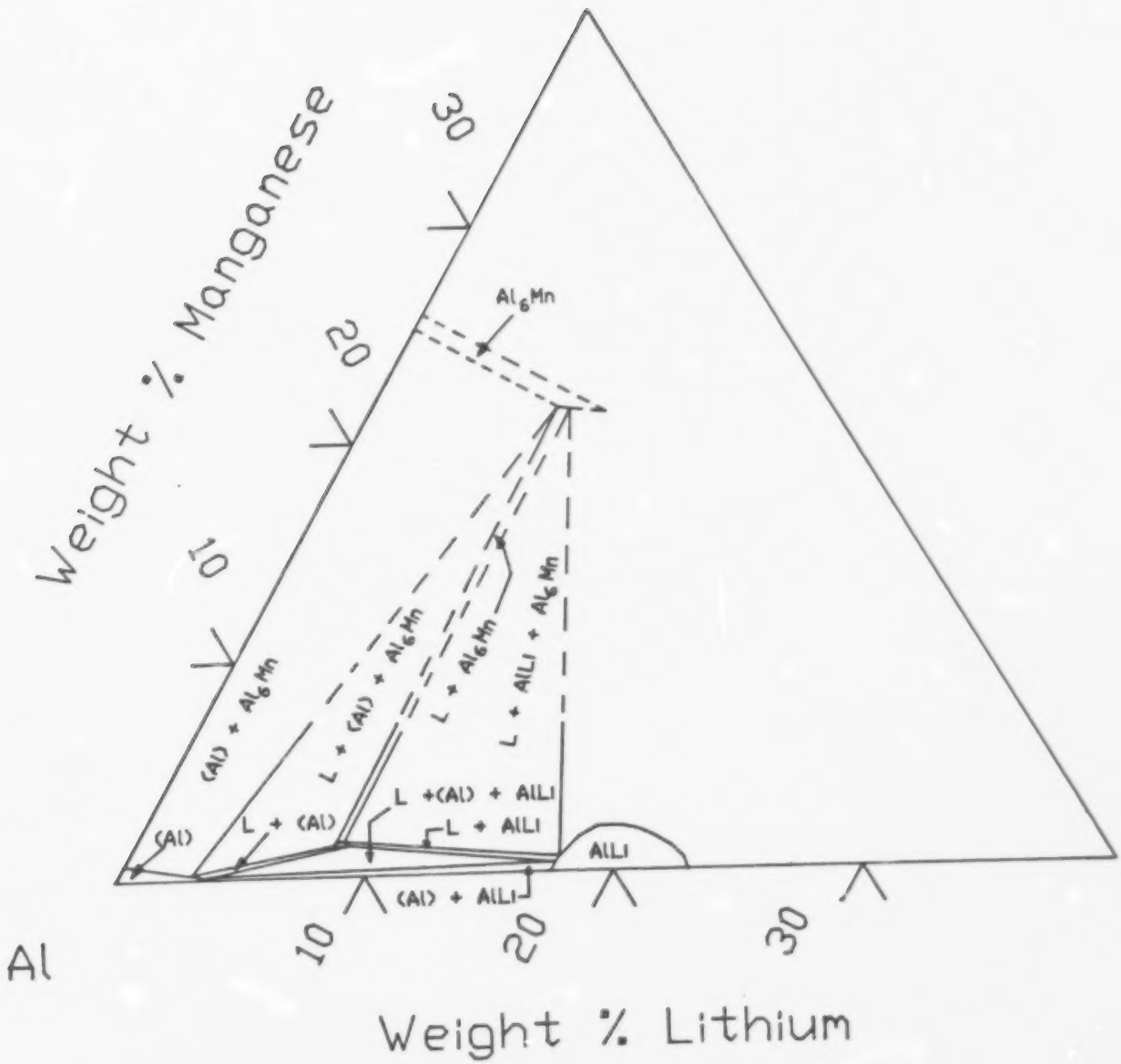

Weight % Manganese
30
20
10
Al_6Mn
(Al) + Al_6Mn
L + (Al) + Al_6Mn
L + Al_6Mn
L + AlLi + Al_6Mn
L +(Al) + AlLi
L + AlLi
(Al)
L + (Al)
AlLi
(Al) + AlLi
Al
10
20
30
Weight % Lithium

Fig. 9a

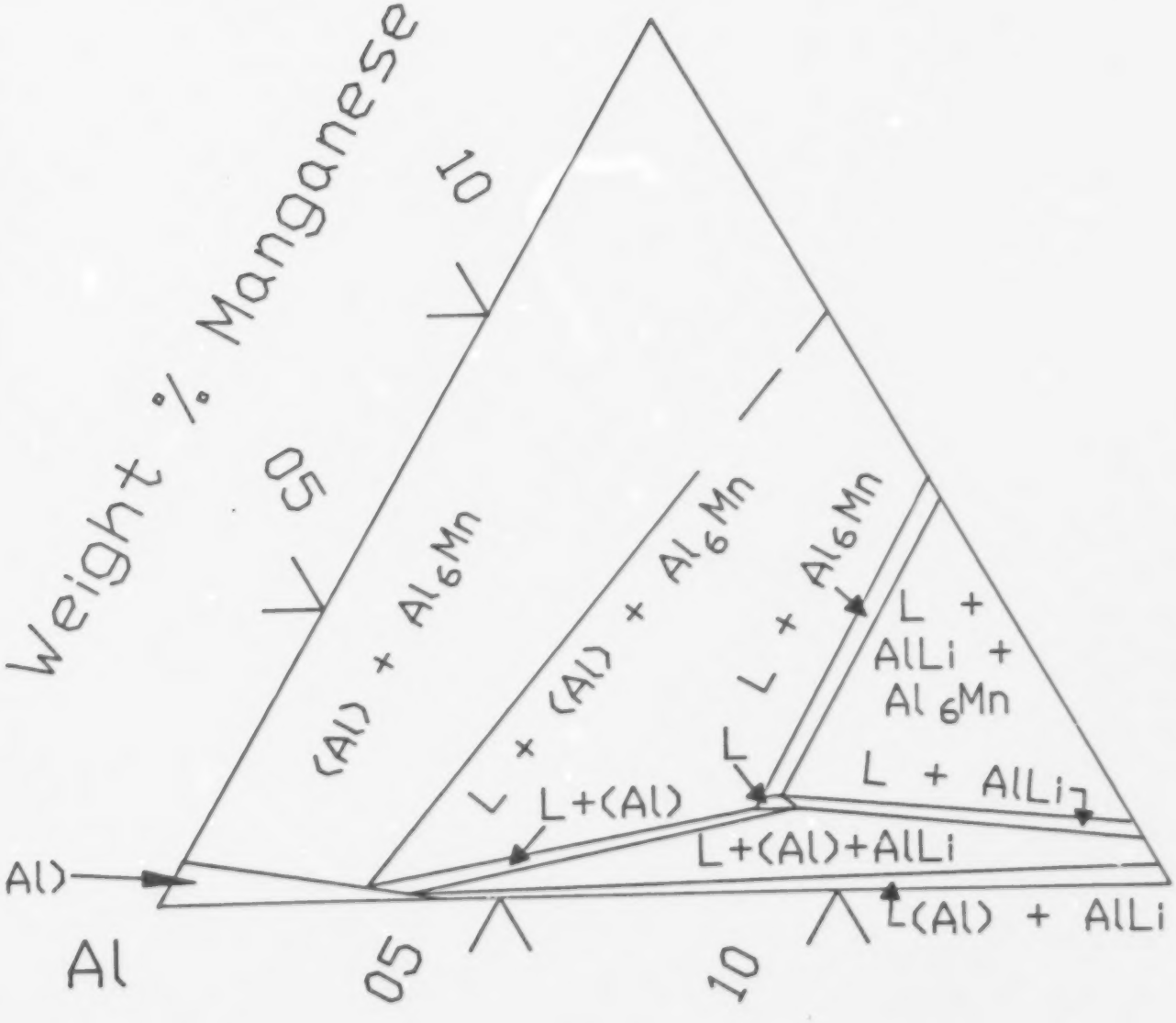

Weight % Manganese
10
50
(Al) + Al6Mn
L + (Al) + Al6Mn
L + Al6Mn
L + AlLi + Al6Mn
L
L + AlLi7
L+(Al)
L+(Al)+AlLi
L(Al) + AlLi
Al)
Al
05
10
Weight % Lithium

Fig. 10

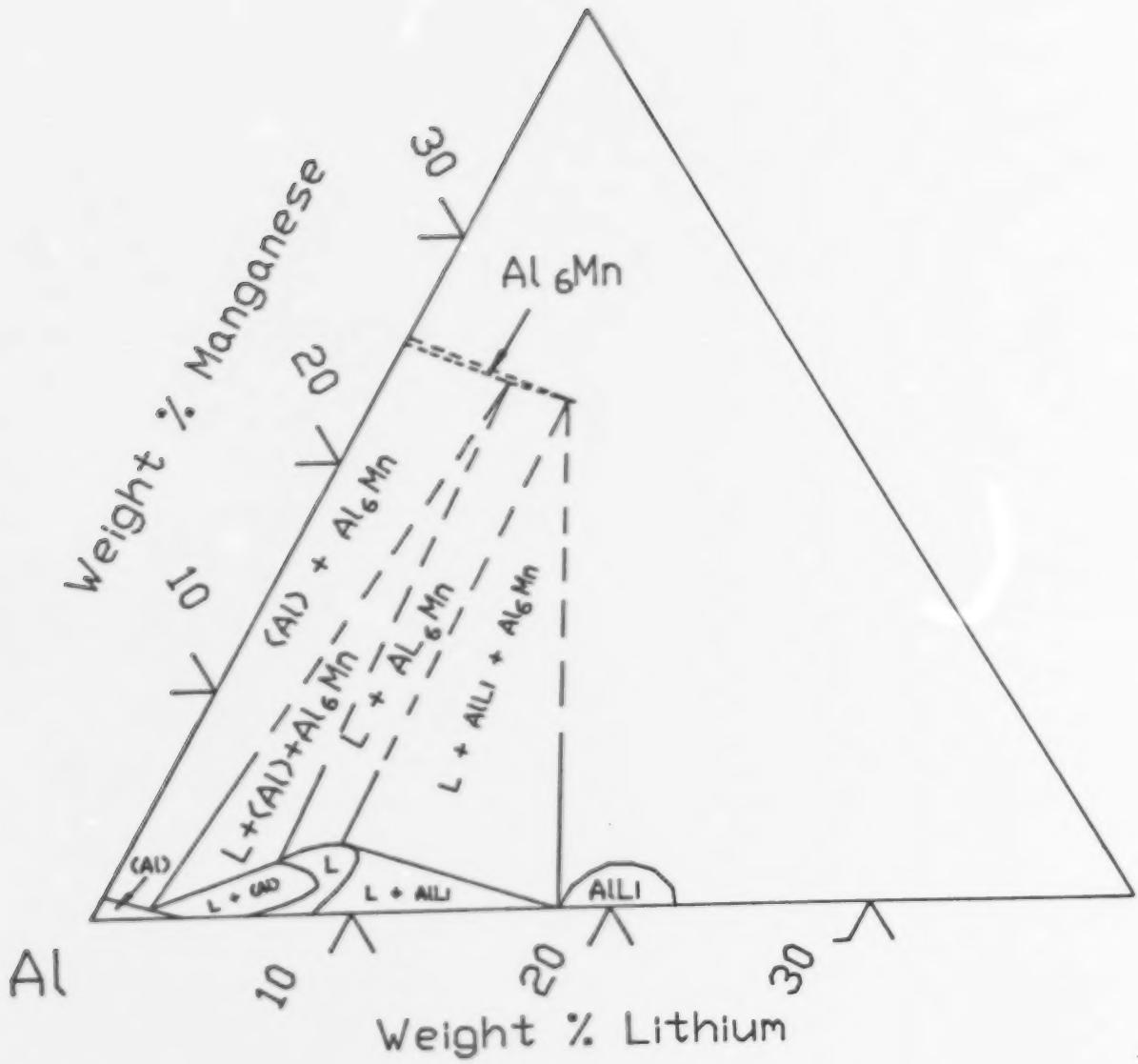

Weight % Manganese
30
20
10
Al 6Mn
(Al) + Al6Mn
L+(Al)+Al6Mn
L + AL6Mn
L + AlLi + Al6Mn
(Al)
L + (Al)
L
L + AlLi
AlLi
Al
10
20
30
Weight % Lithium

Fig. 11

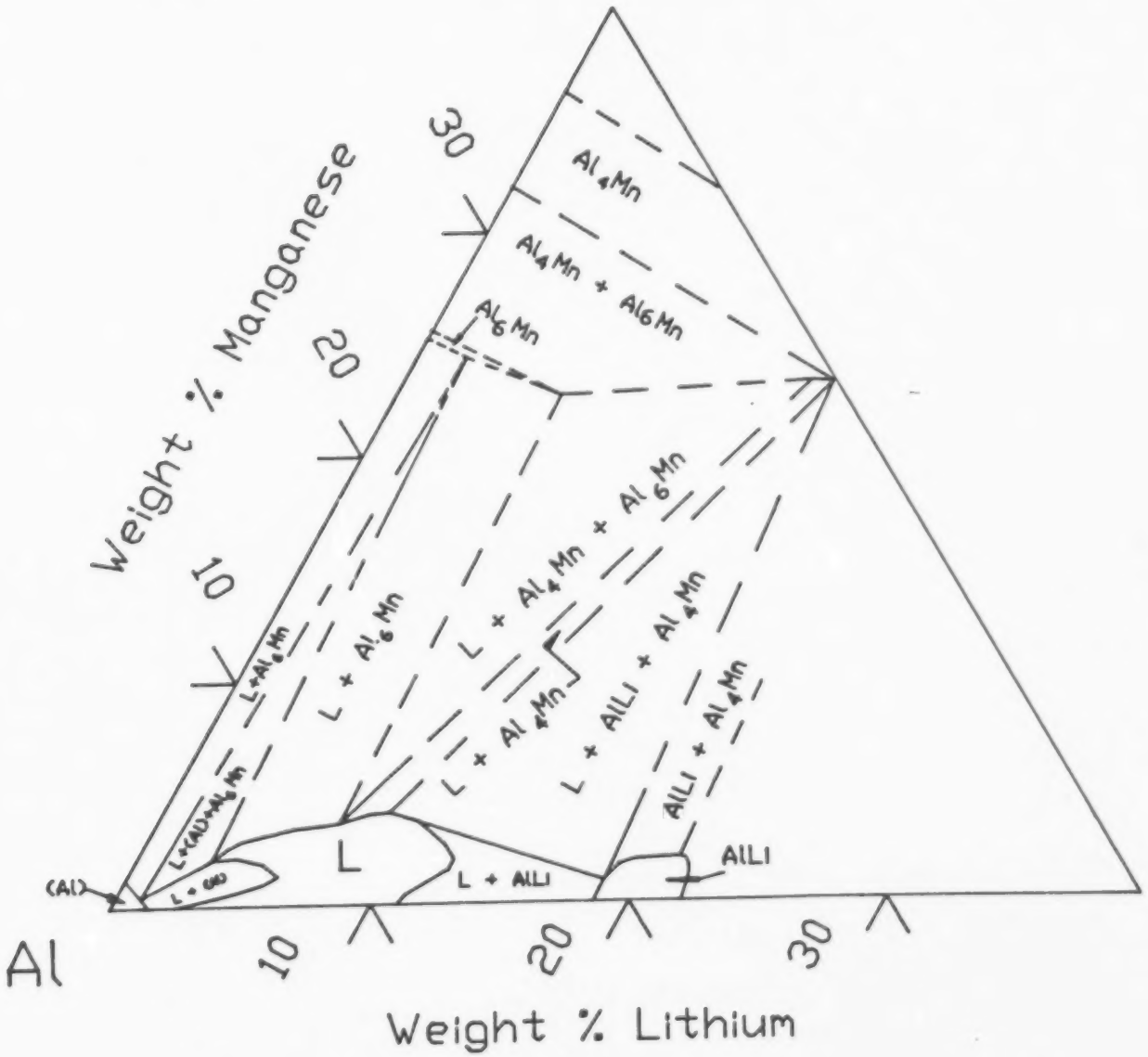
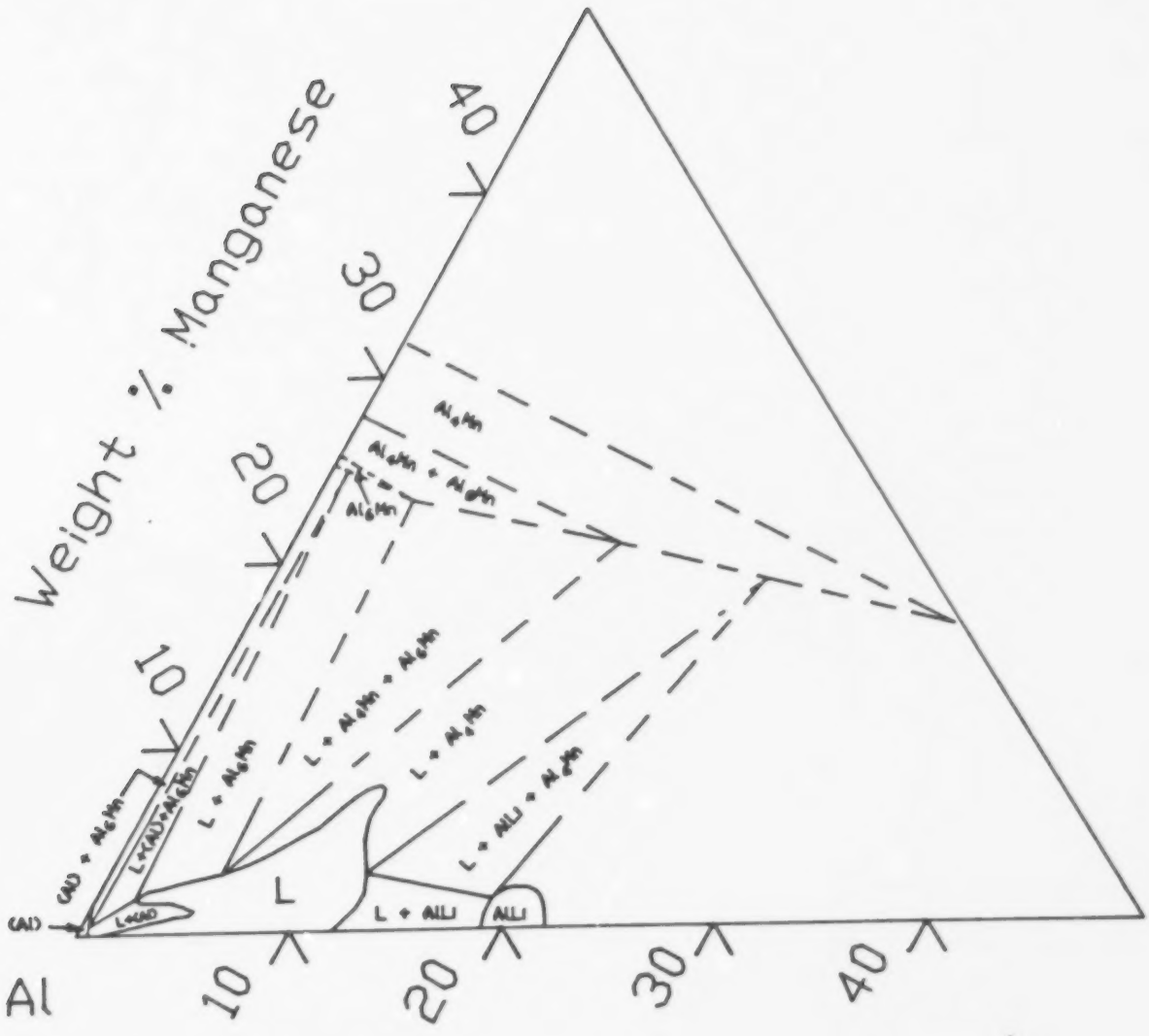

Weight % Manganese
30
20
10
Al
10
20
30
Weight % Lithium
Al4Mn
Al4Mn + Al6Mn
Al6Mn
L + Al6Mn
L + Al4Mn + Al6Mn
L + Al4Mn
L + AlLi + Al4Mn
AlLi + Al4Mn
L
L + AlLi
AlLi
(Al)

Fig. 12


Weight % Manganese
10
20
30
40
Al
10
20
30
40
Weight % Lithium
L
L + AlLi
AlLi
(Al)

Aluminum-Lithium-X Ternary Systems

Part III

The Al-Li-Si (Aluminum-Lithium-Silicon) System

26.98154 6.941 28.0855

The Al-Li-Si System:

Introduction:

The aluminum-rich corner of the Al-Li-Si ternary system has been studied by [84HAN, 76KAD, 67DRI, 49BOO(a,b)]. [76KAD] and [76DRI] have constructed liquidus surface and an isotherm at 550°C for the aluminum-rich corner of this system using high-purity Al, Li and Si and employing thermal and microstructural analysis. However, their diagrams are inconsistent with the current constituent binaries. For example, they have assumed the lithium concentration in the Al-Li eutectic to be between 8.4-9.9 wt/o Li contrary to the value of 7.5 w/o Li as reported by [82McA] in their recent evaluation of Al-Li system. [84HAN]'s study, which is more recent, assumes the Al-Li binary to be at 10 w/o Li.

The purpose of this note is to correlate the existing data for the Al-Li-Si ternary system and make the data consistent with the currently accepted binaries. The liquidus projection and some isothermal sections for this system are also included.

Binary Systems:

The constituent binary phase diagrams for Al-Li, Li-Si and Al-Si are well established as assessed by [82McA], [69SHU] and [84MUR], respectively, and have been adopted as such in this evaluation. Important phases and important reactions (with their compositions) in Al-Li system have been summarized in an earlier note [86GOE]. The reactions for the Li-Si and Al-Si systems are given in this note. The Al-Li eutectic reaction at a composition of 7.5 w/o Li and 600 ± 5°C has been established

by [82McA] and is contrary to the eutectic composition between 8.4-9.9 w/o as reported by [76KAD] and 10 w/o as assumed by [84HAN]. [82McA] tabulates a value of 26 a/o Li for the Al-Li eutectic, but the diagrams show 24 a/o, which has been assumed correct in this communication. In the Li-Si system, the two compounds Li_4Si and Li_2Si are known to form via a peritectic reaction at 635°C and an eutectic reaction at 650°C, respectively, as per the following reactions [69SHU]:

p_1: L(18.25 a/o Si) + Li_2Si (33.25 a/o Si) $\underline{635°C}$ Li_4Si (19.2 a/o Si)

e_1: L(38.9 a/o Si) $\underline{650°C}$ Li_2Si (33.25 a/o Si) + (Si)

[76KAD] has taken the Li-Si eutectic to occur at 635°C. [84MUR] has reported that the Al-Si eutectic occurs at 12.6 w/o Si and 577°C in agreement with [84HAN], but contrary to the eutectic composition of 11.7 w/o Si as reported by [76KAD] as per the reaction

e_2: L (12.2 a/o Si) $\underline{577°C}$ (Al) (1.5 a/o Si) + (Si) (100 a/o Si)

The Al-Li-Si ternary diagram has therefore been altered in the present evaluation to correspond to the most recent binary diagrams.

Ternary Diagrams:

From a study of the solidification of several Al-Li-Si alloys, [49BOO(a,b)] had shown that in these alloys invariant transformations took place at a temperature approximately 8°C lower than that of the Al-Si eutectic (577°C). He has also reported the presence of a ternary compound, as an extension of LiAl up to the formula LiSiAl (11.2 w/o Li and 45.2 w/o Si). [76KAD] and [76DRI] have studied the phase equilibria and phase relationships at the Al-rich corner of the Al-Li-Si system using

high purity alloys with up to 12 w/o Li and Si and employing thermal analysis (under controlled heating and cooling conditions) and microscopy. From the polythermal sections with constant contents of 2.0, 5.0, 7.0 and 11.5 w/o Si; 3.0 and 5.0 w/o Li; 92 w/o Al and sections with a silicon-to-lithium ratio of 2.7 (some of which are shown in Figures 1 to 4), [76KAD] have constructed the liquidus projection which is shown as broken lines in Fig. 5. From their microstructural examination and the thermal analysis results for the polythermal sections, they established the following two eutectic reactions:

E_1: Liquid (11.5 w/o Si and 0.5 w/o Li) $\underline{\underline{565 \pm 3°C}}$ (Al) + (Si) + T

and,

E_2: Liquid (2.0 w/o Si and 9.2 w/o Li) $\underline{\underline{595 \pm 2°C}}$ (Al) + AlLi T

where T is the ternary compound with the approximate chemical formula $Li_3Al_2Si_2$.

[76KAD] have also found a quasi-binary region between the aluminum and the ternary compound; it is a simple eutectic diagram (Fig. 6) with limited solubility in the solid state. The temperature of the eutectic equilibrium is about 635°C, and the concentrations at the eutectic point of Li and Si are 1.5 w/o and 3.8 w/o, respectively.

A liquidus projection from a more recent study by [84HAN] on 40 Al-Li-Si ternary alloys with up to 14 w/o Li and 25 w/o Si are also included in Fig. 5 (shown as continuous lines) for the purpose of comparison with the results of [76KAD]. [84HAN] have reported (as is also clear from Fig. 5) that Al-AlLi binary eutectic is depressed by silicon to a ternary eutectic point, E.1, and the Al-Si binary eutectic is also

depressed by lithium to a ternary eutectic point, E.2, as per the following reactions:

E.1: Liquid (1.1 w/o Si + 10.6 w/o Li) $\underset{\rightleftharpoons}{592°C}$ (Al) + AlLi + a faceted phase which appears to be a ternary compound approximating to AlLiSi.

E.2: Liquid (13.8 w/o Si + 1.4 w/o Li) $\underset{\rightleftharpoons}{575°C}$ (Al) + (Si) + AlLiSi.

Whereas the temperature of the eutectic E_2 of [76KAD] is similar to that of the eutectic E.1 of [84HAN], the compositions are quite different. The temperature and composition both for the other ternary eutectic are differently reported by the two investigators. The composition of the maxima in the monovariant valley at ~ 630°C and 4.0 w/o Li and 5.0 w/o Si of [84HAN] is also different from that of [76KAD] who have reported the same to occur at 1.4 w/o Li and 3.4 w/o Si and 635°C.

The inconsistency in the Si-rich ternary eutectic is due to the difference in the composition of the binary eutectic assumed by [76KAD] and [84HAN]. In view of the correct composition of Al-Si eutectic assumed by [84HAN], their ternary eutectic E.2 in place of the ternary eutectic E_1 of [76KAD] has been taken here to be correct.

The discord in the ternary eutectics E_2 of [76KAD] and E.1 of [84HAN] is primarily due to a wide divergence in the position of the Al-Li binary eutectic. Since the work of [84HAN] is more recent, their liquidus projection with the Al-Li binary eutectic shown at 7.5 w/o Li is tentatively assumed to be correct in this evaluation and is separately shown in Fig. 7 with the liquidus surface isotherms included.

Isothermal Sections:

[76DRI] determined isothermal sections for the Al-rich corner of the Al-Li-Si ternary system from the microscopic examination of the alloys deformed and annealed at 550°C, 500°C and 200°C. Their only isothermal section at 550°C available from their published work is shown in Fig. 8. Using the results of their polythermal sections and forcing agreement with the latest binary systems, we have been unable to construct isothermal sections at temperatures above 600°C which are consistent with the data. For example, for the Al-2% Si section (Fig. 1) in the range 8-12% Li at 610°C the phase field sequence L, L + LiAl, L + (Al) + LiAl does not seem possible. Further, the section for 5% Si in Figure 3 shows the composition Al-5% Si-11% Li to be liquid at temperatures above 600°C. The liquidus temperature for this composition is over 700°C as shown in Fig. 7. However the data presented by [76KAD] appears consistent at Li concentrations below about 8 w/o and an isotherm at 600°C drawn from the data of [76KAD] (Figures 1-4) is shown in Fig. 9.

Regions of Primary Crystallization and Ternary Compounds:

The following phases are reported [84HAN, 76KAD, 76 DRI] to be in equilibrium with the aluminum-based solid solution designated as (Al):

i) α-Si, a silicon-based solid solution, designated as (Si),

ii) a solid solution based on AlLi, and

iii) a ternary compound, designated as AlLiSi, which has been reported by [67PEA] to occur at about equimolar proportions of Al:Li:Si and as having cubic structure (space group Fd3m; 16

atoms per unit cell, lattice parameter ranging from a ≃ 0.594 nm at AlLiSi to a ≃ 0.638 nm at AlLi) as confirmed by x-ray powder diffraction analysis.

These regions of primary solidification are clearly marked in figures 8 and 9.

The solubilities of silicon and lithium in aluminum binary alloys at different temperatures are well established [82McA and 84 MUR]. Additions of silicon and lithium mutually lower the solubility of each other in aluminum. From a close look at the isothermal sections, the general conclusion of [76KAD] and [76DRI] as discussed below are accepted as such in this evaluation: The boundaries of the two-phase regions (Al) + (Si) and (Al) + AlLi are very close to those of the binary systems, indicating little or no homogeneity ranges based on (Si) and AlLi in the ternary system. The (Al) + AlLiSi two-phase range is considerable suggesting a significant homogeneity range based on the ternary compound. The three-phase regions (Al) + (Si) + AlLiSi and (Al) + AlLi + AlLiSi are fairly wide. With decreasing temperature, the single and two-phase regions become much smaller, whereas the three-phase regions become broad.

Conclusions:

From the limited experimental data of [84HAN, 76KAD, 76DRI and 49BOO], the following general conclusions can be drawn concerning the phase relationships at the aluminum corner of the Al-Li-Si system.

1) The phases (Si), AlLi and a ternary phase ≃ AlLiSi are in equilibrium with the aluminum-based solid solution (Al).
2) The ternary compound has the approximate formula AlLiSi instead of $Al_2Li_3Si_2$.

3) There are two ternary invariant eutectic reactions with a maxima in the monovariant valley.

4) Additions of Si and Li mutually lower the solubilities of each other in Al.

5) With decreasing temperature, the extents of single and two-phase regions decrease appreciably, whereas those of three-phase regions widen.

6) There exists a large area of homogeneity based on the ternary compound which decreases appreciably with increasing temperature.

Cited References:

49BOO(a): E.A. Boom, "Physicochemical Investigation of Al-Si-Li Alloys", Dokl. AN SSSR, 67(4), p. 871-74 (1949).

49BOO(b): E.A. Boom, "A New Phase in The Al-Si-Li System", Dokl. AN SSSR, 66(4) p. 645 (1949).

67PEA: W.B. Pearson, Handbook of lattice spacings of Metals and Alloys, Pergamon Press, 2, p. 571 (1967).

69SHU: F.A. Shunk, Constitution of Binary Alloys, Second Supplement, McGraw Hill, N.Y., p. 480 (1969).

76KAD: E.S. Kadaner, N.I. Turkina and V.I. Kuz'mina, "Aluminum-Rich Range of the Al-Si-Li Phase Diagram", Russian Metallurgy, No. 1, pp. 150-53 (1976).

76DRI: M.E. Drits, E.S. Kadaner, V.I. Kuz'mina and N.I. Turkina, "Phase Composition of Aluminum-Rich Al-Si-Li Alloys", Russian Metallurgy, No. 5, pp. 177-78 (1976).

82McA: A.J. McAlister, "The Al-Li (Aluminum-Lithium) System", Bulletin of Alloy Phase Diagrams, 3(2), pp. 177-83 (1982).

84HAN: M.D. Hanna and A. Hellawell, "The Liquidus Surface for the Al-Li-Si System from 0.20 Wt Pct Li and 0.20 Wt Pct Si", Metall. Trans., 15A, pp. 595-97 (1984).

84MUR: J.L. Murray and A.J. McAlister, "The Al-Si (Aluminum-Silicon) System", Bulletin of Alloy Phase Diagrams, 5(1), pp. 74-84 (1984).

86GOE: N.C. Goel and J.R. Cahoon, "Al-Li-Mn System", submitted to Bull. Alloy Phase Diagrams (1986). Also as Part II of this Report.

Figure Captions:

Fig. 1-4. Polythermal sections of the Al-Li-Si Diagram with constant contents of 2 w/o Si (Fig. 1), 5 w/o Li (Fig. 2), 5 w/o Si (Fig. 3), and 92 w/o Al (Fig. 4); after [76KAD].

Fig. 5. Liquidus Projections of [76KAD] (shown as broken lines) and [84HAN] (shown as continuous lines).

Fig. 6. Quasi-binary section of the Al-Li-Si Diagram after [76KAD].

Fig. 7. Speculative Liquidus Projection.

Fig. 8. Isothermal section at 550°C after [76DRI].

Fig. 9. Isothermal section at 600°C.

Fig. 1

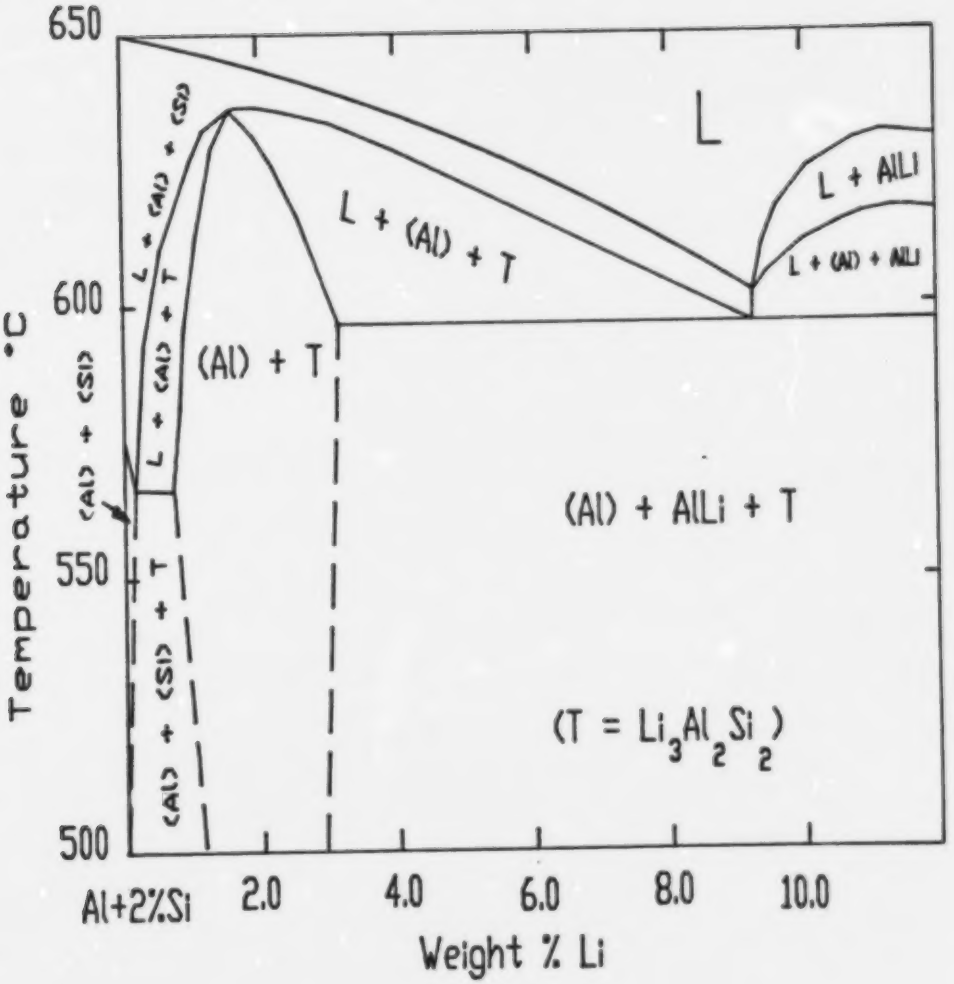

650
600
550
500
Temperature °C
L
L + (Al) + (Si)
L + (Al) + T
L + (Al) + T
L + AlLi
L + (Al) + AlLi
(Al) + (Si)
(Al) + (Si) + T
(Al) + T
(Al) + AlLi + T
(T = Li3Al2Si2)
Al+2%Si
2.0
4.0
6.0
8.0
10.0
Weight % Li

Fig. 2

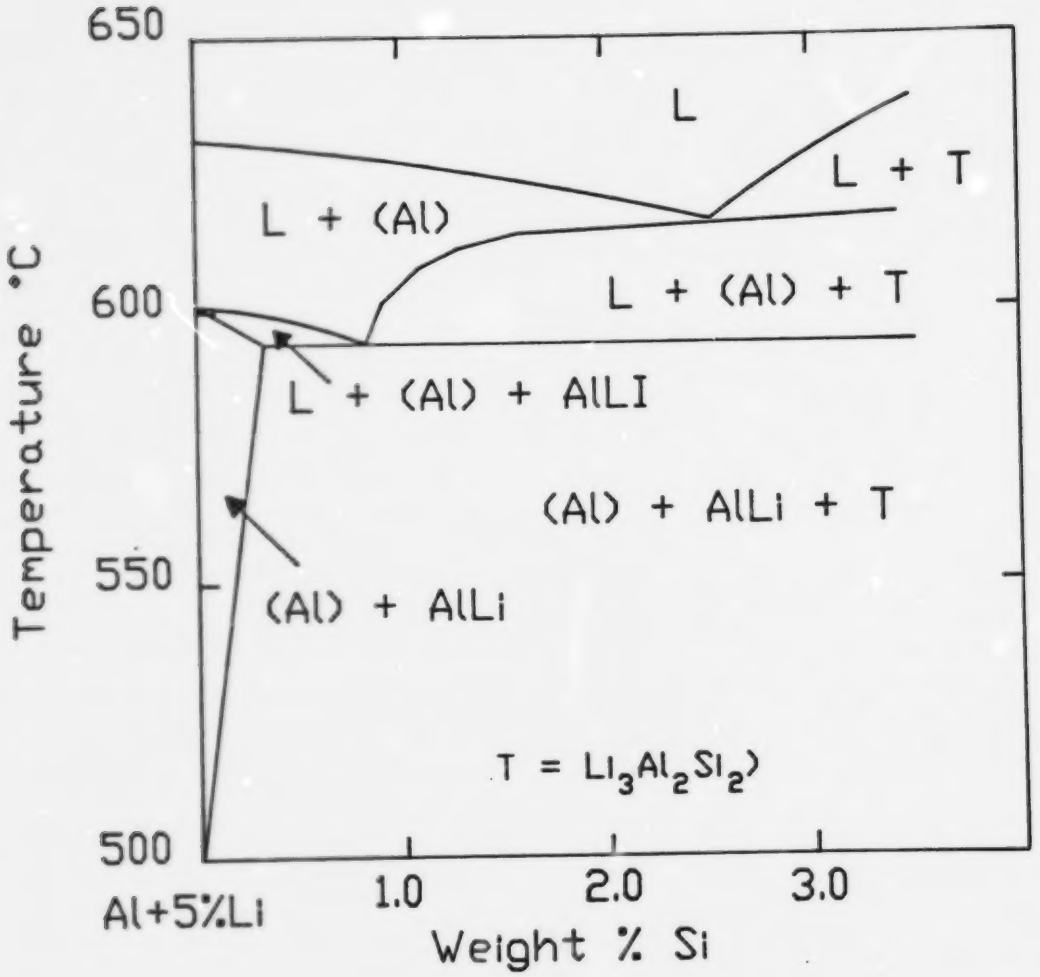

650
600
550
500
Temperature °C
L
L + T
L + (Al)
L + (Al) + T
L + (Al) + AlLI
(Al) + AlLi + T
(Al) + AlLi
T = Li3Al2Si2)
Al+5%Li
1.0
2.0
3.0
Weight % Si

Fig. 3

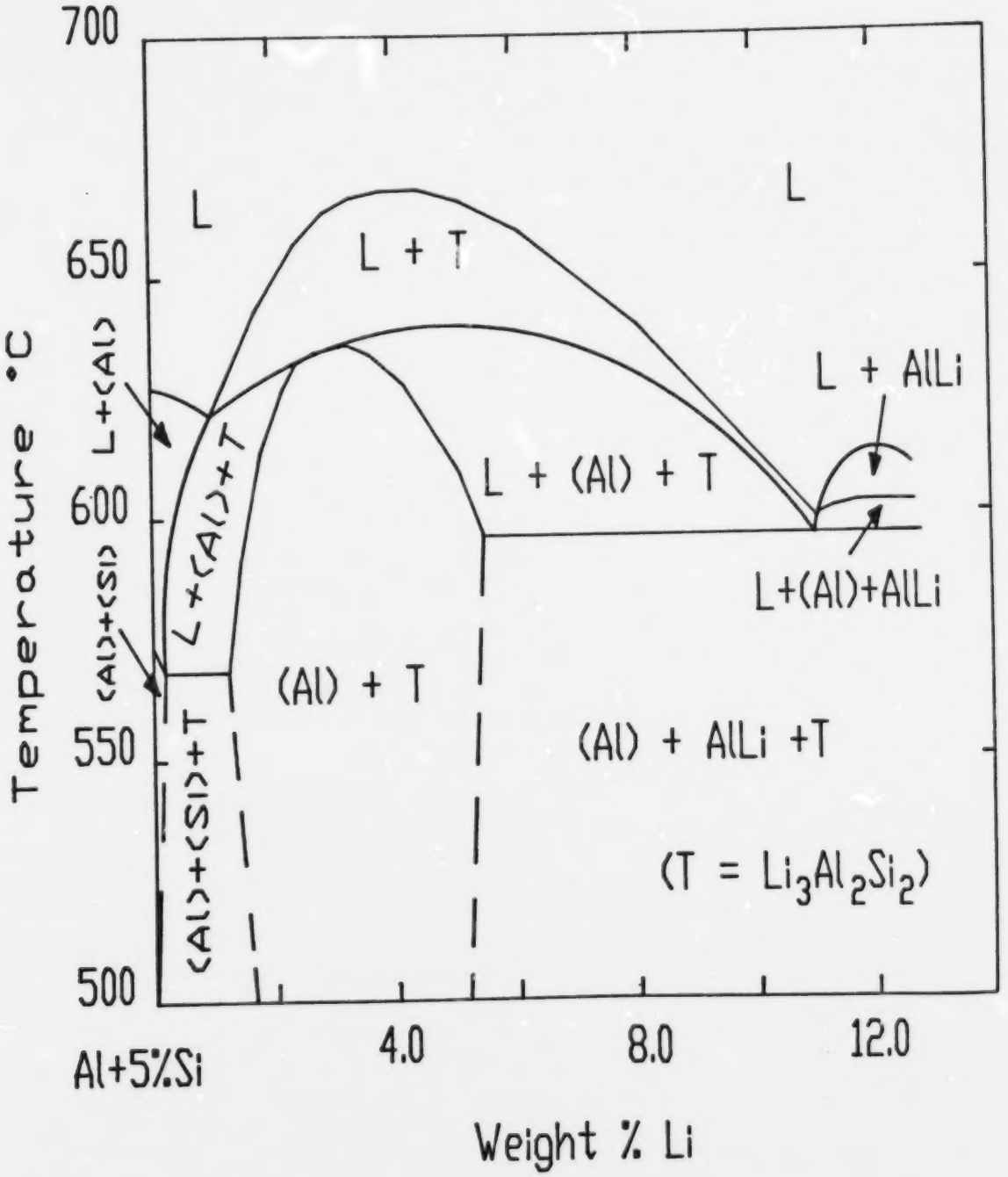

700
650
600
550
500
Temperature °C
L
L + T
L
L + AlLi
L + (Al) + T
L+(Al)+AlLi
L+⟨Al⟩
⟨Al⟩+⟨Si⟩
L+⟨Al⟩+T
⟨Al⟩+⟨Si⟩+T
(Al) + T
(Al) + AlLi +T
(T = Li3Al2Si2)
Al+5%Si
4.0
8.0
12.0
Weight % Li

Fig. 4

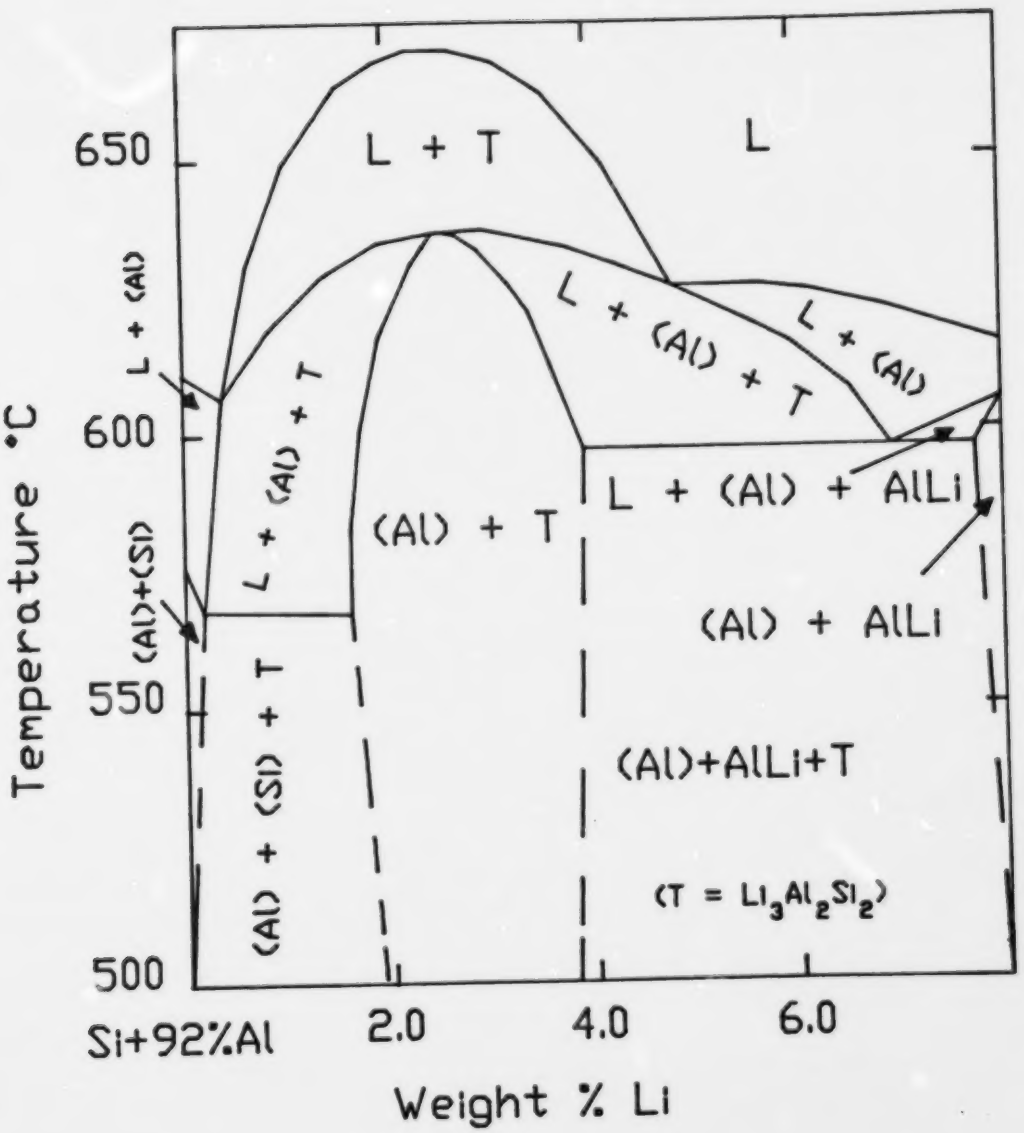

650
600
550
500
Temperature °C
L + T
L
L + (Al)
L + (Al) + T
L + (Al) + T
L + (Al)
(Al) + T
L + (Al) + AlLi
(Al)+(Si)
(Al) + AlLi
(Al) + (Si) + T
(Al)+AlLi+T
(T = Li3Al2Si2)
Si+92%Al
2.0
4.0
6.0
Weight % Li

Fig. 5

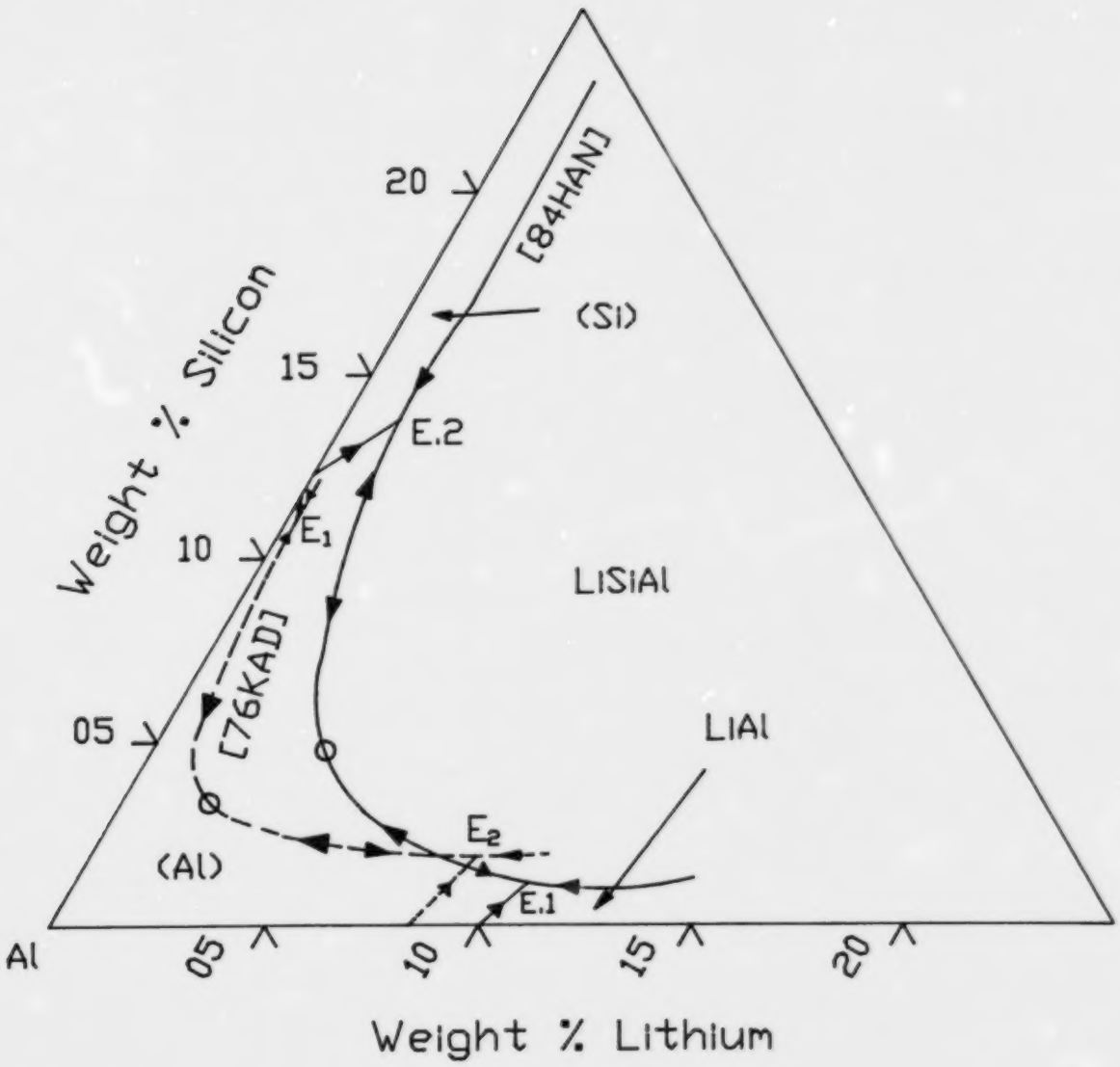

20
15
10
05
Al
05
10
15
20
Weight % Silicon
Weight % Lithium
[84HAN]
(Si)
E.2
E₁
LiSiAl
[76KAD]
LiAl
E₂
(Al)
E.1

Fig. 6

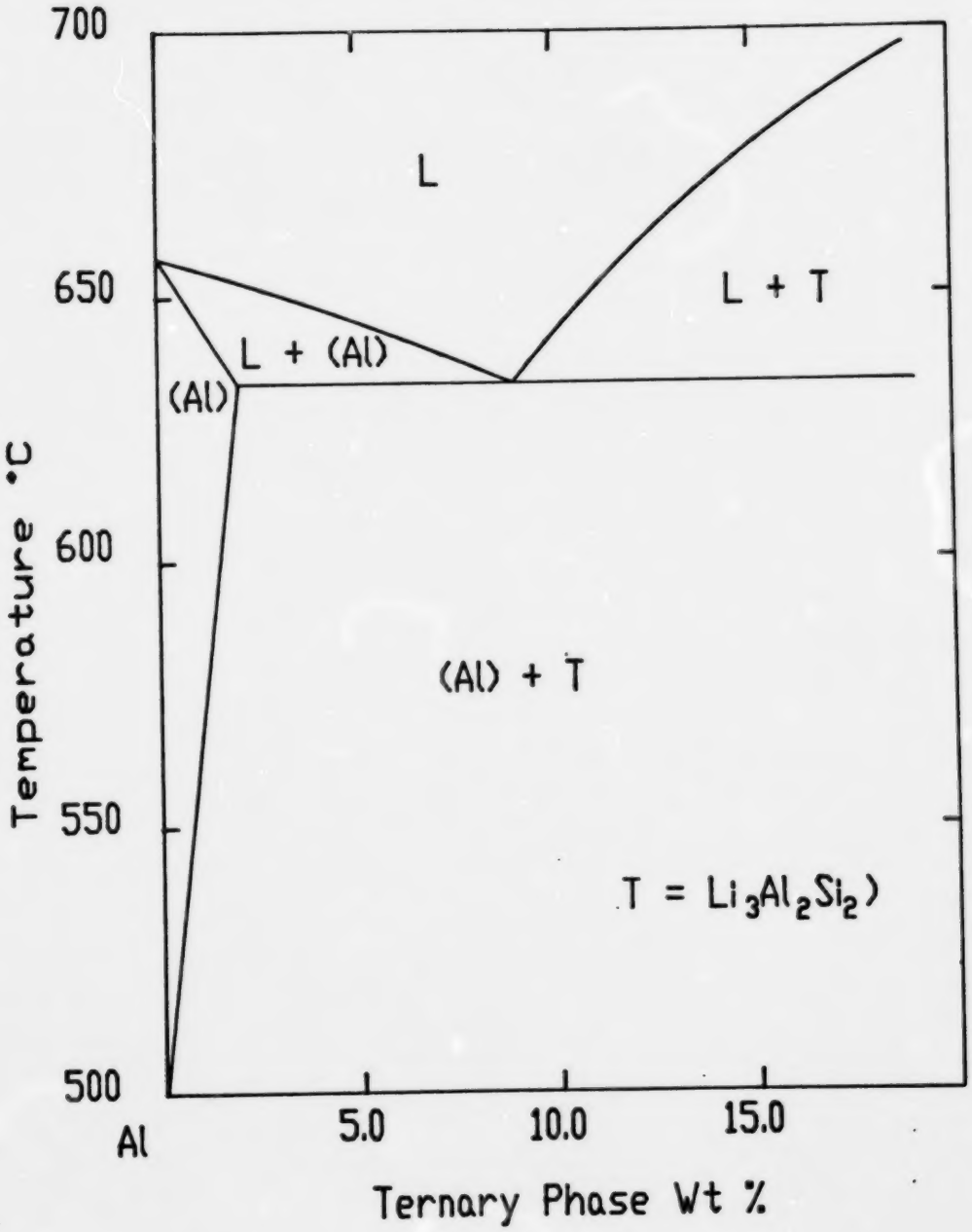

700
650
600
550
500
Temperature °C
L
L + T
L + (Al)
(Al)
(Al) + T
T = $Li_3Al_2Si_2$)
Al
5.0
10.0
15.0
Ternary Phase Wt %

Fig. 7

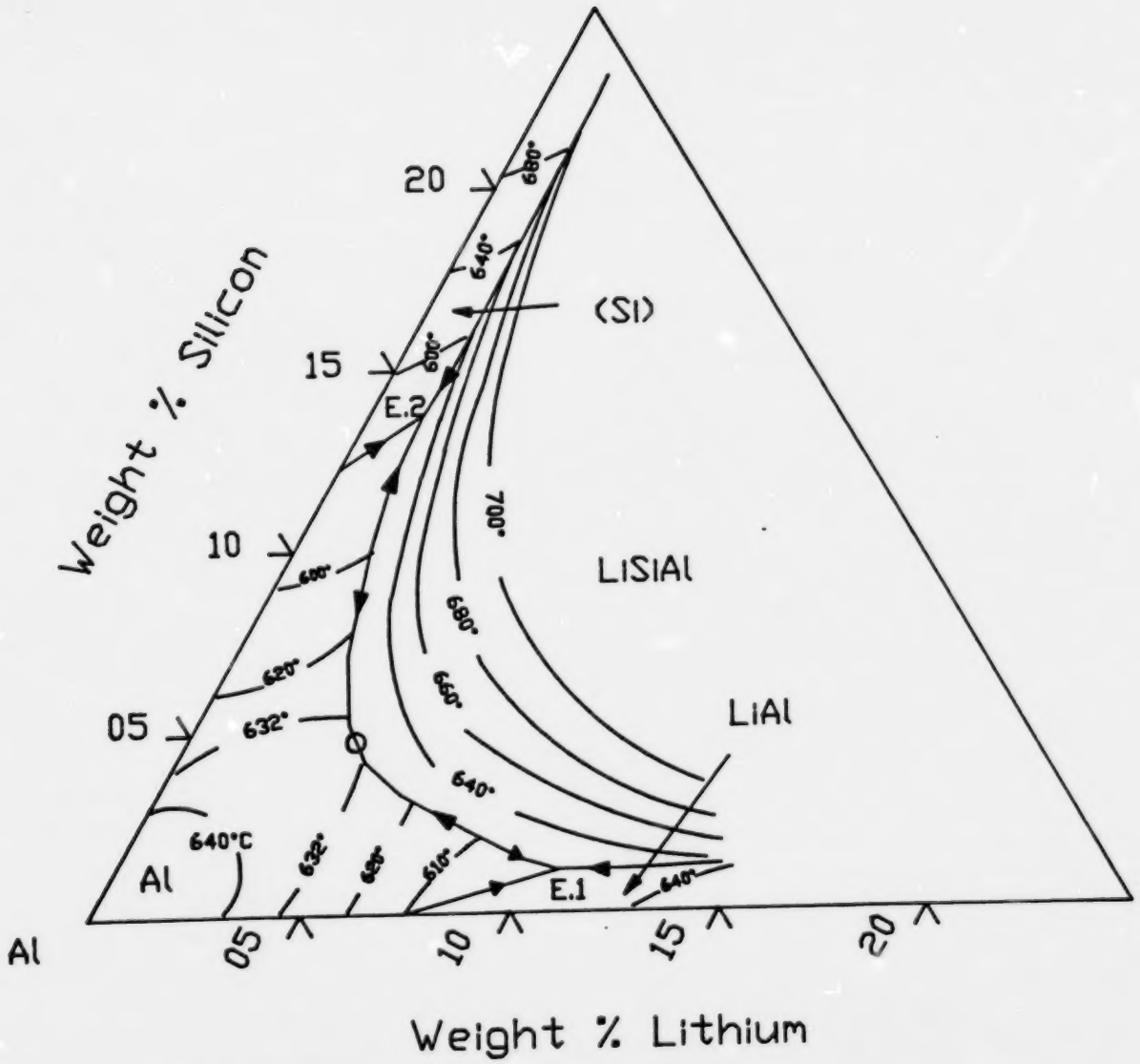

Weight % Silicon
20
15
10
05
Al
05
10
15
20
Weight % Lithium
(SI)
LISIAl
LiAl
Al
E.1
E.2
640°C
632°
620°
610°
600°
640°
680°
700°
650°

Fig. 8

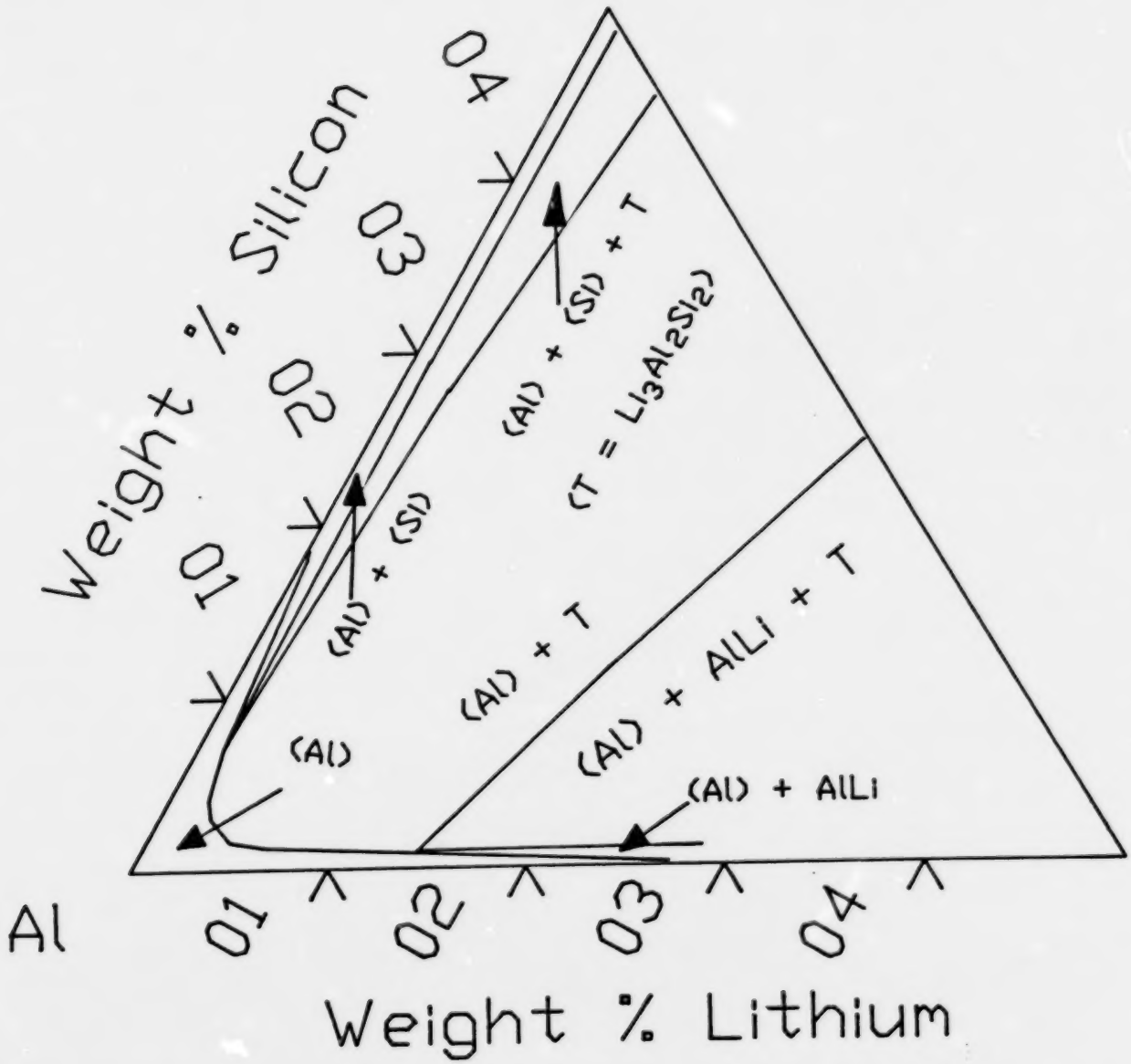
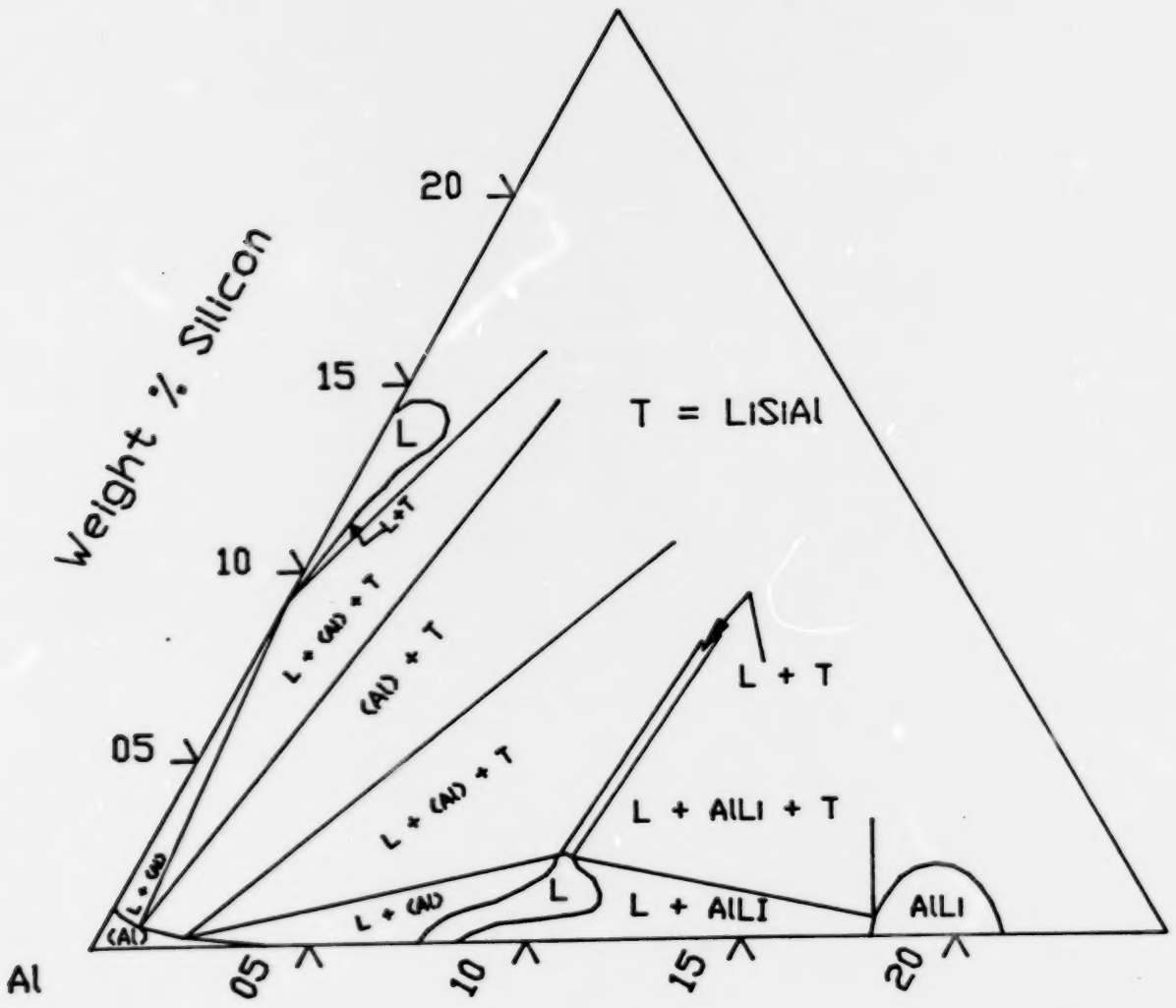

Weight % Silicon
10
20
30
40
(Al) + (Si) + T
(T = Li3Al2Si2)
(Al) + (Si)
(Al) + T
(Al) + AlLi + T
(Al)
(Al) + AlLi
Al
01
02
03
04
Weight % Lithium

Fig. 9


Weight % Silicon
20
15
10
05
T = LiSiAl
L
L+T
L + (Al) + T
(Al) + T
L + (Al) + T
L + T
L + AlLi + T
L + (Al)
L
L + AlLi
AlLi
(Al)
L + (Al)
Al
05
10
15
20
Weight % Lithium

The Aluminum-Lithium-X Ternary Systems

Part IV

The Al-Li-Zn (Aluminum-Lithium-Zinc) Ternary System

26.98154 6.941 65.38

Introduction

The equilibrium phase relationships in Al-Li-X ternary systems have not been widely studied despite the importance of these alloys as strong, light materials. The literature available on these systems is rather old and therefore the equilibrium ternary phase diagrams for these systems need to be reassesed particularly in light of recent information on the constituent binary systems. A critical evaluation of the Al-Li-Mg, Al-Li-Mn, Al-Li-Si, Al-Li-Cu systems, and several other Al-Li-X systems where no information is available even to construct partial diagrams is included in Parts I, II, III, V and VI respectively of this report. In this part, a critical assessment of the Al-Li-Zn ternary system is prsented in the light of the available experimental literature and the most recent constituent binaries. From a review of the literature it was found that the nature of different phases (which are often denoted by ambiguous symbols without specifying their chemical formula) and the reported equivalent phase relationships in the Al-Li-Zn system are very unclear. Also, the data are inconsistent with the recent binary systems.

In this assessment of the Al-Li-Zn ternary system the most recent Al-Li, Al-Zn and Li-Zn binary systems adopted in this evaluation are reviewed along with the experimental results of [43BAD1] and [64CHE] on the Al-Li-Zn ternary system. A speculative liquidus projection and some representative isothermal sections are reconstructed from the data of [43BAD1] and [64CHE] but forcing agreement with the accepted binaries. The phase fields are clearly identified with their symbols and appropriate chemical formulae.

Binary Systems:

The three constituent binary systems Al-Li, Li-Zn and Al-Zn pertaining to the Al-Li-Zn ternary system are fairly well established as assessed by [82McA], [58HAN] and [83MUR], respectively, and have been adopted as such in this evaluation. Important phases and important reactions (with their

composition) in the Al-Li system have been summarized in our earlier evaluation of the Al-Li-Mg and Al-Li-Mn Systems [86GOE].

The three-phase equilibria and pure metal transformations that define the topology of the Al-Zn binary diagram according to the most recent assessment by [83MUR] are summarized below:

L (88.7)	$\underset{\text{Eutectic}}{\overset{381°C}{\rightleftharpoons}}$	(α'Al) (67.0) + (Zn) (97.2)
(α'AL) (59.0)	$\underset{\text{Eutectoid}}{\overset{277°C}{\rightleftharpoons}}$	(α AL) (16.5) + (Zn) (98.4)
AL(39.5)	$\underset{\text{Critical}}{\overset{351.5°C}{\rightleftharpoons}}$	(α Al) + α'(Al)
L (0.0)	$\underset{\text{Congruent}}{\overset{660.452°C}{\rightleftharpoons}}$	(Al)
L (100.0)	$\underset{\text{Congruent}}{\overset{419.58°C}{\rightleftharpoons}}$	(Zn)

The figures in brackets give the compositions in at. % Zn.

There are no intermetallic compounds in this system and the (Al) liquidus and solidus descend to a eutectic equilibrium with cph (Zn) at 381°C. The two-phase region, proposed in Murray's assessment [83MUR], does not agree with the previous determinations of the miscibility gap. This two-phase region which separates two structurally identical fcc solid solution phases of nearly equal compositions seems thermodynamically implausible.

The Li-Zn binary phase diagram of [33GRU] with some supplements and a few changes at lower temperatures by [35ZIN] remains the most accepted to date [86MAS] as reported in the evaluation of this system by [58HAN]. Of the eight intermediate phases δ, δ", δ', $LiZn_2$, Y, Y', β and β' originally reported by [33GRU], existence of five intermediate room temperature phases δ" (LiZn), δ' (Li_2Zn_3), $LiZn_2$, Y'(Li_3Zn_7 - Li_2Zn_5) and β' ($LiZn_4$) was confirmed by [35ZIN]. Two eutectic reactions, one each at the Li-rich and

Zn-rich corners respectively, and two peritectic reactions as listed below can be easily identified from the Li-Zn binary given by [58HAN]:

$$L(4.5) \underset{\text{Eutectic}}{\overset{161°C}{\rightleftharpoons}} \text{Li } (2.0) + \delta' (50.0),$$

$$L(96.0) \underset{\text{Eutectic}}{\overset{403°C}{\rightleftharpoons}} \text{Zn } (98.5) + \beta (91.5),$$

$$L (80.0) + \gamma (73.0) \underset{\text{Peritectic}}{\overset{481°C}{\rightleftharpoons}} \beta (91.5), \text{ and}$$

$$L + \delta (67.0) \underset{\text{peritectic}}{\overset{502°C}{\rightleftharpoons}} \gamma (71.0)$$

Where the figures in brackets are the compositions in atomic percent zinc. At room temperature, the primary solid solutions are of negligible extent in this system. The crystallographic data for the binary phases is given in Table 1.

Ternary Diagrams:

The only studies available on the Al-Li-Zn ternary system are those by [43BAD1, 43BAD2, 43BAD3, 42WEI, 52SHA and 64CHE]. Of these, only [42WEI], [52SHA] and [64CHE] are concerned with the determination of the aluminum-zinc side of the ternary diagram and identification of ternary phases and reactions. Other studies deal mainly with the mechanical properties of Al-Li-Zn alloys.

Using thermal analysis, chemical analysis and metallography, [43BAD1] have constructed two vertical quasi-binary sections AlLi-Li_2Zn_3 (Fig. 1) and Zn-AlLi (Fig. 2), in addition to eight other sections (section I to section VIII) in the partial system of Al-Zn-AlLi with Zn:Li ratios varying between 11:1 and 1:30 (Figs. 3 - 10).

The AlLi-Li_2Zn_3 Section (Fig. 1) was typical of solid solutions with single phase microstructures over the whole section.

The liquidus of the vertical section Zn-AlLi (Fig. 2) consisted of four branches corresponding to the crystallization of β, γ, δ and ε Phases, each

having a variable composition. The β Phase, which is a solid solution of Al and Li in Zn and represented by (Zn) in this evaluation, forms a eutectic at 369°C with 11.25% Li and 11.25% Al. The γ and δ phases form peritectically from the δ and the melt at 490°C, and from the ε and the melt at 580°C respectively. The δ Phase is a triple solid solution based upon the AlLi Compound. [64CHE] have reported this δ Phase to be identical with their Al-Li-Zn ternary compound. Therefore, this δ phase has been taken as the only ternary compound reported for this system.

In their section with Zn:Li ratio = 11:1 (Fig. 3), the liquidus descends continuously from pure Al to (Zn + Li) = 86.5 at % (79.3 at % Zn + 7.2 at % Li), where the double eutectic of α' + β begins to crystallize at 375°C. At 355°C and (Zn+Li) = 88.45% (81.08 at % Zn + 7.37 at % Li), α' + β + γ eutectic crystallizes. The nature of their α' phase, however, is not understood. It may be similar to the α' (Al) solid solution of the presently accepted Al-Zn binary. The peritectic reaction at 440°C, which is termed by [43BAD1] as a continuation of the peritectic process in the Al-Zn System, is inconsistent with the present Al-Zn binary where there is no peritectic reaction. The transformation in the solid state at 270°C could be a continuation of the eutectoidal transformation in the Al-Zn system.

Primary crystallization of α and transformation of delta phase to γ phase at 368°C and at Zn + Li = 68% (54.4 at % Zn + 13.6 at % Li), and a reaction at 315°C in the region Of 25 - 43% (Zn + Li) in the solid state are shown in their section with a Zn:Li ratio = 4:1 (Fig. 4).

The section with a Zn:Li ratio = 3:2 (Fig. 5) hits the quasi-binary section Zn-AlLi (Fig. 2) in the δ region, the delta forming by a peritectic reaction at 580°C.

Several of their other sections (shown in Figs. 6 - 10) are fairly simple in nature.

Liquidus Surface: From these various vertical sections, [43BAD1] have constructed the liquidus surface mainly in the Al-Zn-AlLi triangle which is shown in Fig. 11. They have established the existence of a triple eutectic of $\alpha+\beta+\gamma$ at 355°C and three other transitional points at 368°C, 423°C and 452°C respectively as shown in Fig. 11 and which are listed in Table 2. In the light of the most recent constitutent binaries as adopted in the present evaluation, the following inconsistencies and confusions concerning the phase fields in the liquidus projection of (43BAD1) are apparent:

1) It is now established that other than the eutectic reaction at the Zn-rich corner, there is no peritectic reaction in the Al-Zn binary system at 70.0 at % Zn as reported by [43BAD1].
2) In the ternary eutectic reaction L 355°C $\alpha + \beta + \gamma$, the phase fields α, β, γ are confusing. They have perhaps represented their phases based on, ZnAl, (Zn), and $Li_2 Zn_5$ by α, β and γ respectively.
3) They have not reported any ternary compound which has been obtained and characterized by (64CHE).

[79MON] have constructed a modified version of the liquidus projection based on the data of [43BAD1] and [42WE1]. Their speculative liquidus projection, converted from weight percent to atomic percent is shown in Fig. 12 and their modified invariant ractions are included in Table 2. Although the phase fields are clearly identifiable from their diagram, the Al-Zn peritectic at 68.0 at % Zn is inconsistent with the present binary. To incorporate the existence of the ternary compound $(AlZn)_2Li$ as reported by [64CHE], the introduction of an additional eutectic reaction L $\xrightarrow{567°C}$ (Al) + AlLi + $(AlZn)_2$ Li by (79 MON), although reasonable, is purely speculative. Also, the compositions of the other invariant reactions

reported by [79MON] are not consistent with the experimental data of [43BAD1]. Furthermore, their invariant reaction temperatures (Table 2) are arbitrarily chosen and the phase field β(LiZn) should in fact be β ($LiZn_4$) to be consistent with the Li-Zn binary.

A modified speculative liquidus projection which has been constructed in the present work using the experimental data of [43BAD1] and incorporating the most recent constitutent binaries is shown in Fig. 13. This diagram not only retains the original experimental data points of [43BAD1] for different invariant reactions, but also agrees well with the most recent Al-Li, Al-Zn and Li-Zn binaries. The speculative portions of this projection however, have been drawn by broken lines. The probable invariant reactions and their compositions as seen from Fig. 13 are also listed in Table 2.

Ternary Compound:

While studying the compounds of the structural type $(AlZn)_{49}\ Mg_{32}$ in Al-Li-Cu and Al-Li-Zn ternary systems, [64CHE] have reported the existence of a ternary compound of approximate chemical formula $(AlZn)_2$ Li in the Al-Li-Zn system. As reported by them, this compound is similar in microstructure and composition to the δ phase of [43BAD1] which has an approximate composition $Al_{35}\ Li_{35}\ Zn_{30}$ at 20°C. However, [43BAD1] have not identified this as a ternary phase. In their detailed study of this ternary compound using x-ray lattice spacing measurements, [64CHE] were unable to obtain this compound in its pure form. The compound has a wide range of existence: from Li $Zn_{0.5}\ Al_{1.5}$ (50.0 at % Al, 33.3 at % Li) to Li $Zn_{1.3}\ Al_{0.7}$ (23.4 at % Al, 33.3 at % Li) as determined by their lattice

spacing measurements. According to them, this ternary compound belongs to the family of compounds $Cu\ Li_3\ Al_5$, $Cu\ Mg_4\ Al_6$ and $(Al\ Zn)_{49}\ Mg_{32}$ and has a cubic structure; space group Im3; 162 atoms to the unit cell; lattice parameter varying from 1.393 to 1.402 nm (Table 1).

Solid State Equilibria and Isothermal Sections:

[43BAD1] have reported the following phases in the aluminum-corner to be in equilibrium: an α-ternary zinc and lithium solid solution in aluminum, the ε-phase - a solid solution based on the compound LiAl, the δ-phase formed from the ε-phase and the mother liquor by a peritectic reaction at 580°C, the γ - Phase formed from the δ-phase and the mother liquor by a peritectic reaction at 490°C and a β-solid solution of aluminum and lithium in zinc. Their isothermal sections at 20°C and 350°C are shown in Figs. 14 and 15 respectively. According to [79MON], who have constructed an isothermal section at 327°C (Fig. 16), aluminum can be in equilibrium with the ternary compond $(AlZn)_2\ Li$, LiAl, ZnAl and Li_2Zn_5.

Based on the data of [43BAD1] and the recent binaries, we have constructed three isothermal sections at 20°C, 325°C and 354°C which represent the phase relationships in the Al-Li-Zn system reasonably well. Also these diagrams are consistent with the presently accepted binary systems. From these isothermal sections, the following phase relationships in the aluminum-corner can be established.

At 20°C: (Al) is in equilibrium with ε (LiAl), τ ($(AlZn)_2\ Li$), γ' ($Li_2\ Zn_5$) and (Zn).

At 325°C: (Al) is in equilibrium with ε (LiAl), τ $(AlZn)_2\ Li$), γ ($Li_2\ Zn_5$) and α' (Al).

At 354°C: (Al) is in equilibrium with ε (LiAl), τ ($(AlZn)_2Li$), $\gamma(Li_2Zn_5)$ and (Zn).

The phase fields in the Zn-rich corner, which are drawn as broken lines in these figures, are speculative.

Solid Solubility Limits: [43BAD1] have also studied the limits of solid solubility of zinc and lithium in aluminum. From their experimental data, the maximum combined solid solubility of (Zn + Li) in aluminum is 16.5 at % (5% Zn + 11.5% Li) at 565°C, which decreases with decreasing temperature.

TABLE 1: Phases and their crystal structure in Al-Li-Zn Ternary System and its Constituent Binaries.

Phase/(Temp.°C)	Symbols used in literature/Ref.	Approximate Composition (at/o)	Pearson Symbol or Crystallographic Structure/Space Group	Prototype	Lattice Parameters in nm a	b	c	Comments
Al-Li Binary System								
Al-Solid Solution < 660.5°C	α[82McA]	0-15 Li	cF4/ Fm3m	Cu	0.40495*	-	-	*At 0 at/o Li
AlLi < 700°C	β[82McA]	45-55 Li	cF16/ Fd3M	NaTl	0.637**	-	-	**At 50 a/o Li
Al_2Li_3 < 520°C	γ[82McA]	60-61 Li	hR15/ R3m	-	0.4508	-	1.426	
Al_4Li_9 < 275°C	δ[82McA]	Line Compound at 69.2 Li	mC2 6/ C2/m	-	1.91551	0.54288	0.44988	β = 107.67
Al_4Li_9 (275-330°C)	δ'[82McA]	69.2 Li	unclassified	-	-	-	-	
Li-Solid[a] Solution < 180.6°C	(Li)[82McA]	100.0 Li	C I2/ IM 3m	W	-	-	-	
Al_3Li Metastable	α'[82McA]	-	CP4/ Pm3n	-	-	-	-	

TABLE 1: Continued

Phase/(Temp.°C)	Symbols used in literature/Ref.	Approximate Composition (at/o)	Pearson Symbol or Crystallographic Structure/Space Group	Prototype	Lattice Parameters in n m a	b	c	Comments
Al-Zn Binary System [83MUR] (No compounds are found in this system)								
α(Al)	(Al) [83MUR]	0-67 Zn	cF4/Fm3m	Cu	0.4046*	-	-	* for 4.45 at % Zn at room Temperature
(α'Al)	(α'Al) [83MUR]	60-70 Zn	Rhombohedral/ R3M	-	-	-	-	
(Zn)	(Zn) [83MUR]	97.2-100 Zn	hP2/ $P6_3/mmc$	Mg	-	-	-	
Li-Zn Binary System [58HAN]								
LiZn <177°C	δ" [35ZIN]	-	CF16/$Fd\bar{3}M$	Natl.	0.6232	-	-	
Li_2Zn_3 <174°C	δ' [35ZIN]	-	c*5	-	0.427	-	-	
$LiZn_2$ <93°C	[35ZIN]	-	-	-	-	-	-	
Li_2Zn_5 <168°C	δ' [35ZIN]	-	hexagonal pseudo cell hp*	-	0.4371	-	2.515	
$LiZn_4$ <245°C	β' [35ZIN]	-	hP2	Mg	0.2788		0.4394	c/a = 1.576 (89.5 at % Zn)
Al-Li-Zn Ternary System:								
$(AlZn)_2Li$	τ [64CHE]	$LiZn_{0.5}Al_{1.5}$ to $LiZn_{1.3}Al_{0.7}$	Cubic/IM3	$(AlZn)_{49}Mg_{32}$	1.393 to 1.402	-	-	

TABLE 2: Invariant Reactions in the Al-Li-Zn System

Sl. No.	Reaction	Composition at % Al	Li	Zn	Remarks
Reference [43BAD1]					
1.	$L \xrightarrow[355°C]{\text{Eutectic}} \alpha + \beta + \gamma$	13.0	8.2	78.8	α, β, Y perhaps refer to ZnAl, (Zn) and Li_2Zn_5 based phases respectively.
2.	$L + \delta \xrightarrow[368°C]{} \beta + \gamma$	14.6	9.7	75.7	δ is reported by them as a triple solid solution based upon the AlLi compound.
3.	$L + (Al) \xrightarrow[423°C]{} \beta + \delta$	24.7	11.7	63.6	
4.	$L + (\varepsilon) \xrightarrow[452°C]{} (Al) + \delta$	33.6	17.4	49.0	ε is also described by them as a solid solution based unpo the AlLi compound.
Reference [79MON]: Probable invariant reactions:					
1.	$L \xrightarrow[567°C]{\text{Eutectic}} Al + LiAl + \tau$	64.2	23.4	12.4	τ is the ternary compound $(AlZn)_2 Li$.
2.	$L + \tau \xrightarrow[447°C]{} (Al) + Li_2Zn_5$	42.6	13.1	44.3	
3.	$L + (Al) \xrightarrow[422°C]{} ZnAl + Li_2Zn_5$	30.63	13.22	56.15	
4.	$L + Li_2Zn_5 \xrightarrow[367°C]{} ZnAl + \beta(LiZn)$	17.7	8.5	73.8	
5.	$L \xrightarrow[342°C]{\text{eutectic}} ZnAl + (Zn) + \beta\,(LiZn)$	9.4	4.3	86.3	
Present Work: Probable invariant reactions:					
1.	$L \xrightarrow[355°C]{\text{Eutectic}} (Al) + (Zn) + LiZn_4$	13.0	8.2	78.8	
2.	$L + Li_2Zn_5 \xrightarrow[368°C]{} (Al) + LiZn_4$	14.6	9.7	75.7	
3.	$L + Li_2Zn_3 \xrightarrow[423°C]{} (Al) + Li_2Zn_5$	24.7	11.7	63.6	
4.	$L + \tau \xrightarrow[452°C]{} (Al) + Li_2Zn_3$	33.6	17.4	49.0	Where τ is the ternary compound $(AlZn)_2Li$.
5.	$L \xrightarrow[?]{\text{Eutectic}} (Al) + AlLi + \tau$		?		This reaction is purely speculative.

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86MAS: Massalski, T.B. (Ed.), Binary Alloy Phase Diagrams, Vol. 2, P. 1509 (1986).

Figure Captions:

Fig. 1 Quasi Binary Section AlLi-Li_2Zn_3 of the Al-Li-Zn System, after [43BAD1].

Fig. 2 Quasi Binary Section Zn-AlLi of the Al Li-Zn System, after [43BAD1].

Fig. 3 Section I: Vertical Section with Zn:Li = 11:1 in the Partial System Al-Zn-AlLi, after [43BAD1].

Fig. 4 Section II: Vertical Section with Zn:Li = 4:1 in the Partial System Al-Zn-AlLi, after [43BAD1].

Fig. 5 Section III: Vertical Section with Zn:Li = 3:2 in the Partial Triangle Al-Zn-AlLi, after [43BAD1].

Fig. 6 Section IV: Vertical Section with Zn:Li = 3:7 in the Partial Triangle Al-Zn-AlLi, after [43BAD1].

Fig. 7 Section V: Vertical Section with Zn:Li = 1:4 in the Partial Triangle Al-Zn-AlLi, after [43BAD1].

Fig. 8 Section VI: Vertical Section With Zn:Li = 1.5:7 in the Partial Triangle Al-Zn-AlLi, after [43BAD1].

Fig. 9 Section VII: Vertical Section with Zn:Li = 1:12 in the Partial Triangle Al-Zn-AlLi, after [43BAD1].

Fig. 10 Section VIII: Vertical Section with Zn:Li = 1:30 in the Partial Triangle Al-Zn-AlLi, after [43BAD1].

Fig. 11 Projection of the Liquidus in the Al-Li-Zn System, after [43BAD1].

Fig. 12 Speculative Liquidus Projection of the Al-Li-Zn System, after [79MON].

Fig. 13 Speculative Liquidus Projection of the Al-Li-Zn System, Present Work.

Fig. 14 Isothermal Section at 20°C in the Partial System Al-Zn-AlLi, after [43BAD1].

Fig. 15 Isothermal Section at 350°C in the Partial System Al-Zn-AlLi, after [43BAD1].

Fig. 16 Speculative Isothermal Section at 327°C in the Al-Li-Zn System after [79MON].

Fig. 17 Speculative Isotherm at 20°C, Present Work.

Fig. 18 Speculative Isotherm at 325°C, Present Work.

Fig. 19 Speculative Isotherm at 354°C, Present Work.

FIG. 1

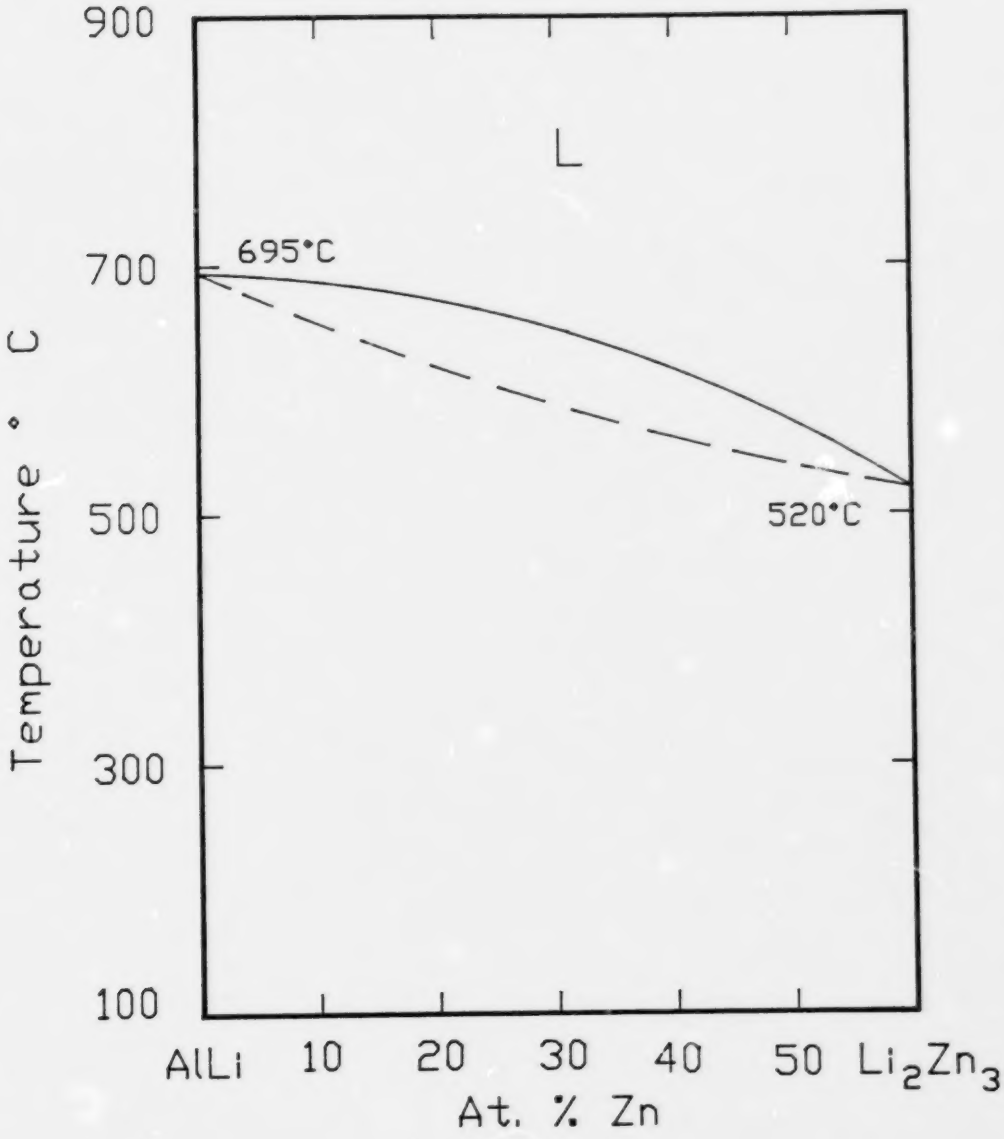

900
700
500
300
100
L
695°C
520°C
Temperature ° C
AlLi
10
20
30
40
50
Li_2Zn_3
At. % Zn

FIG. 2

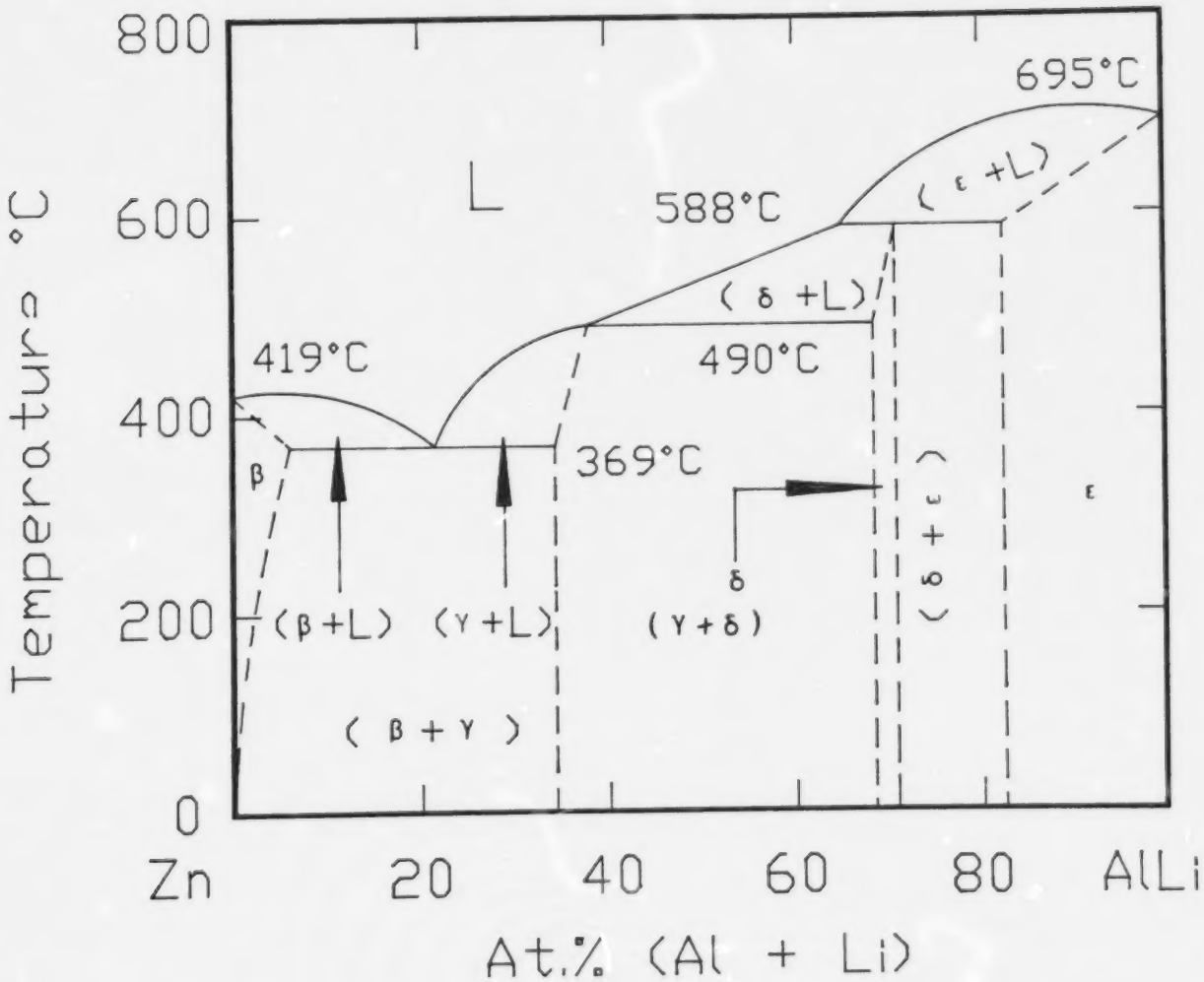

800
600
400
200
0
Temperatura °C
L
695°C
588°C
(ε+L)
(δ+L)
490°C
419°C
369°C
β
(β+L)
(γ+L)
(β+γ)
δ
(γ+δ)
(δ+ε)
ε
Zn
20
40
60
80
AlLi
At.% (Al + Li)

FIG. 3

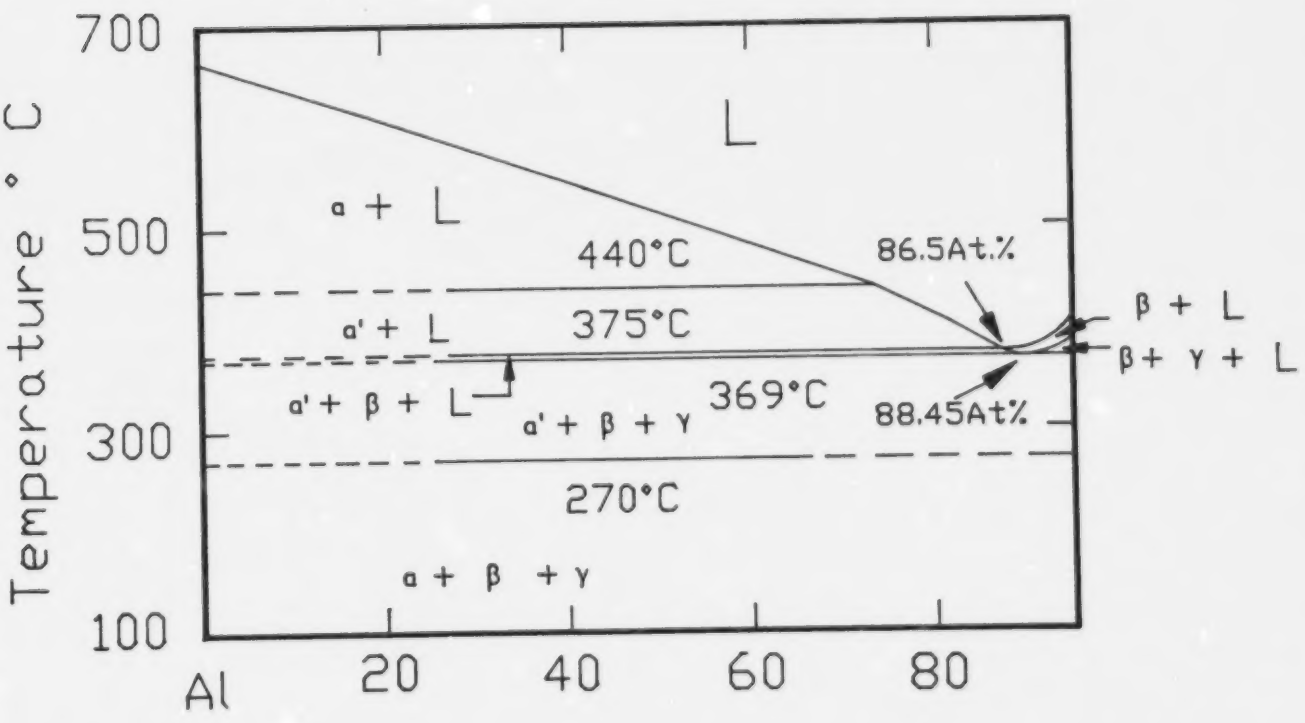

700
500
300
100
Temperature ° C
L
α + L
440°C
86.5At.%
β + L
α' + L
375°C
β + γ + L
α' + β + L
α' + β + γ
369°C
88.45At%
270°C
α + β + γ
Al
20
40
60
80
At.%(Zn+Li) Zn:Li = 11:1

FIG. 4

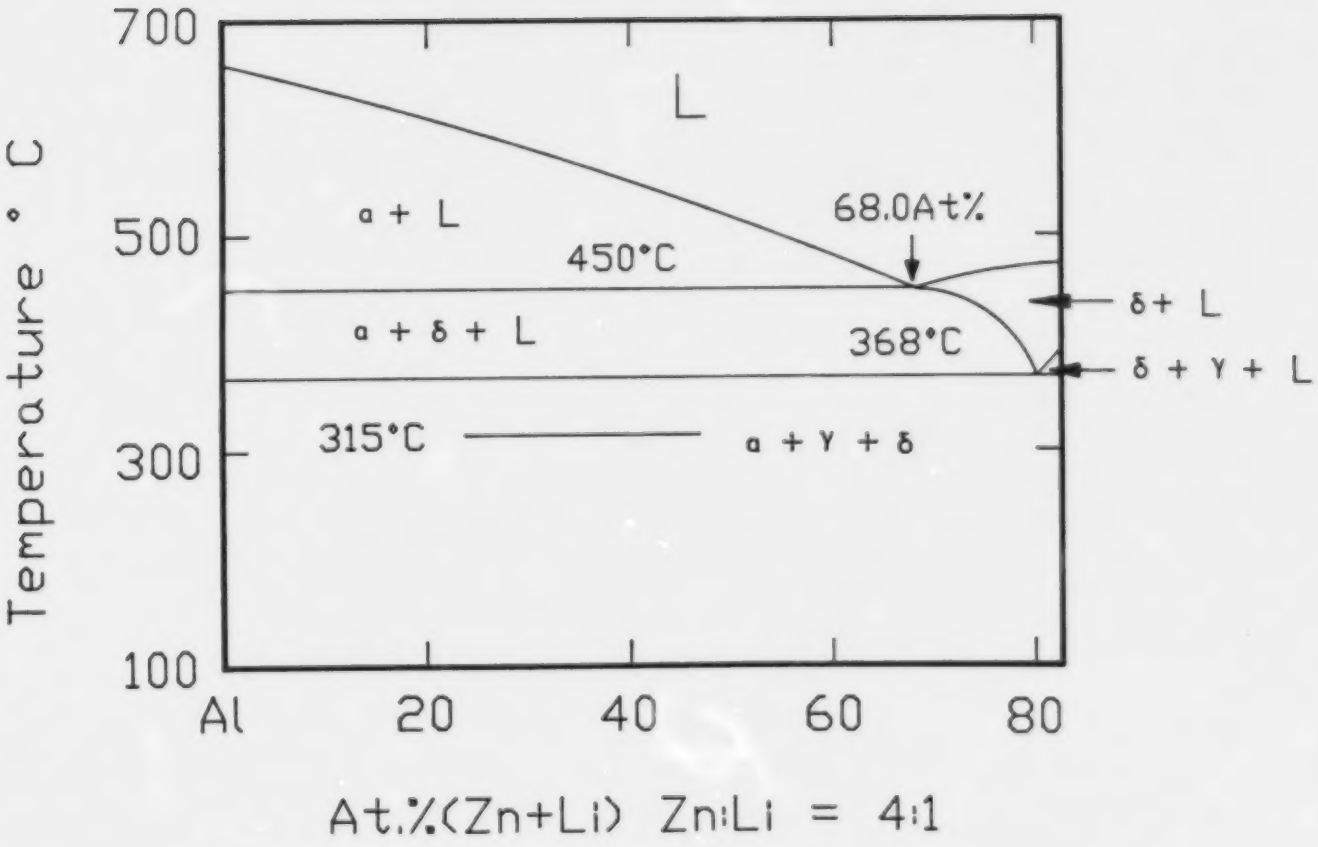

700
500
300
100
Al
20
40
60
80
Temperature ° C
L
α + L
68.0At%
450°C
α + δ + L
368°C
δ+ L
δ + γ + L
315°C
α + γ + δ
At.%(Zn+Li) Zn:Li = 4:1

FIG. 5

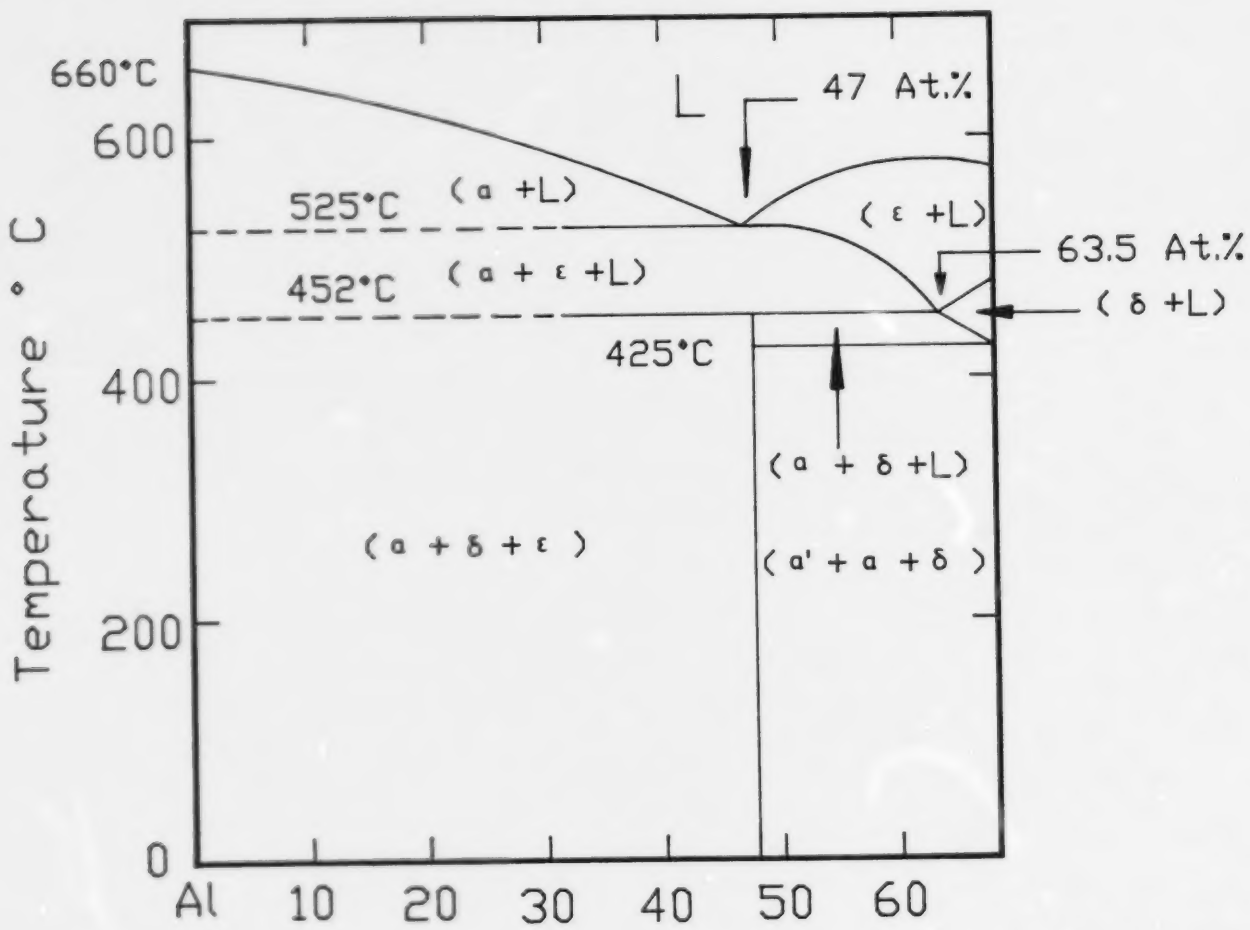

660°C
600
400
200
0
Temperature ° C
L
47 At.%
525°C
(a +L)
(ε +L)
63.5 At.%
452°C
(a + ε +L)
(δ +L)
425°C
(a + δ +L)
(a + δ + ε)
(a' + a + δ)
Al
10
20
30
40
50
60
At>%(Zn+Li) Zn:Li = 3:2

FIG. 6

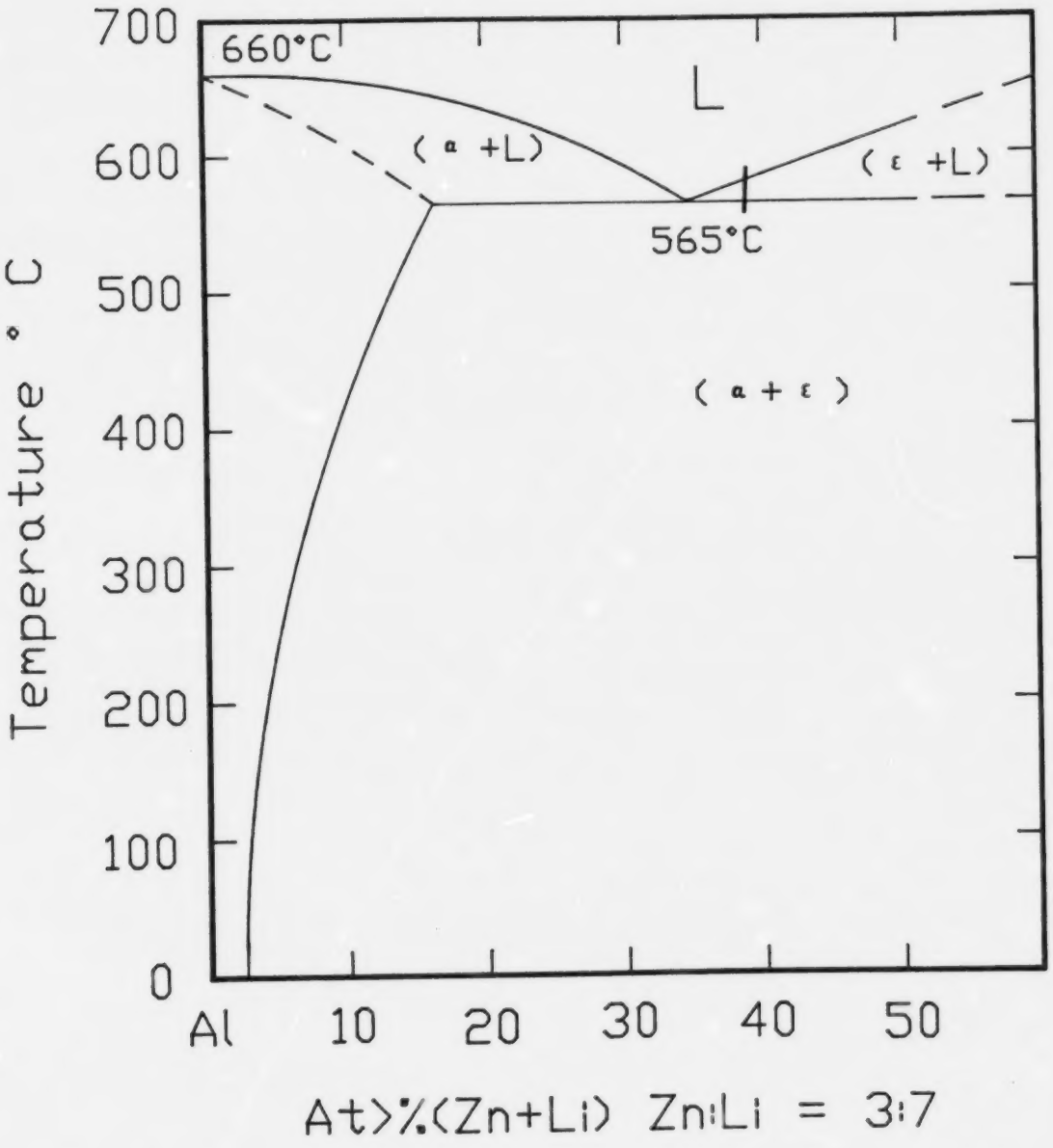

700
600
500
400
300
200
100
0
660°C
L
(α +L)
(ε +L)
565°C
(α + ε)
Temperature ° C
Al
10
20
30
40
50
At>%(Zn+Li) Zn:Li = 3:7

FIG. 7

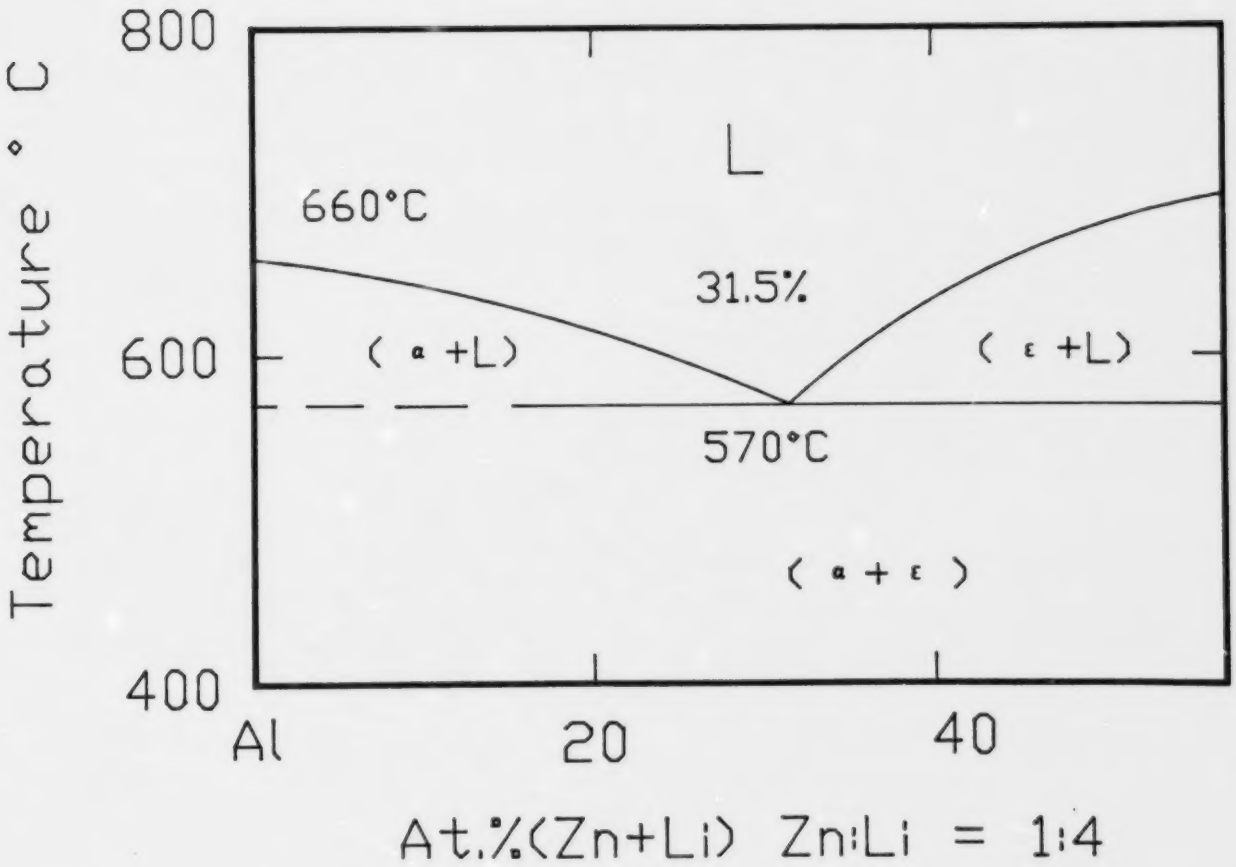

800
600
400
Temperature ° C
L
660°C
31.5%
(α +L)
(ε +L)
570°C
(α + ε)
Al
20
40
At.%(Zn+Li) Zn:Li = 1:4

FIG. 8

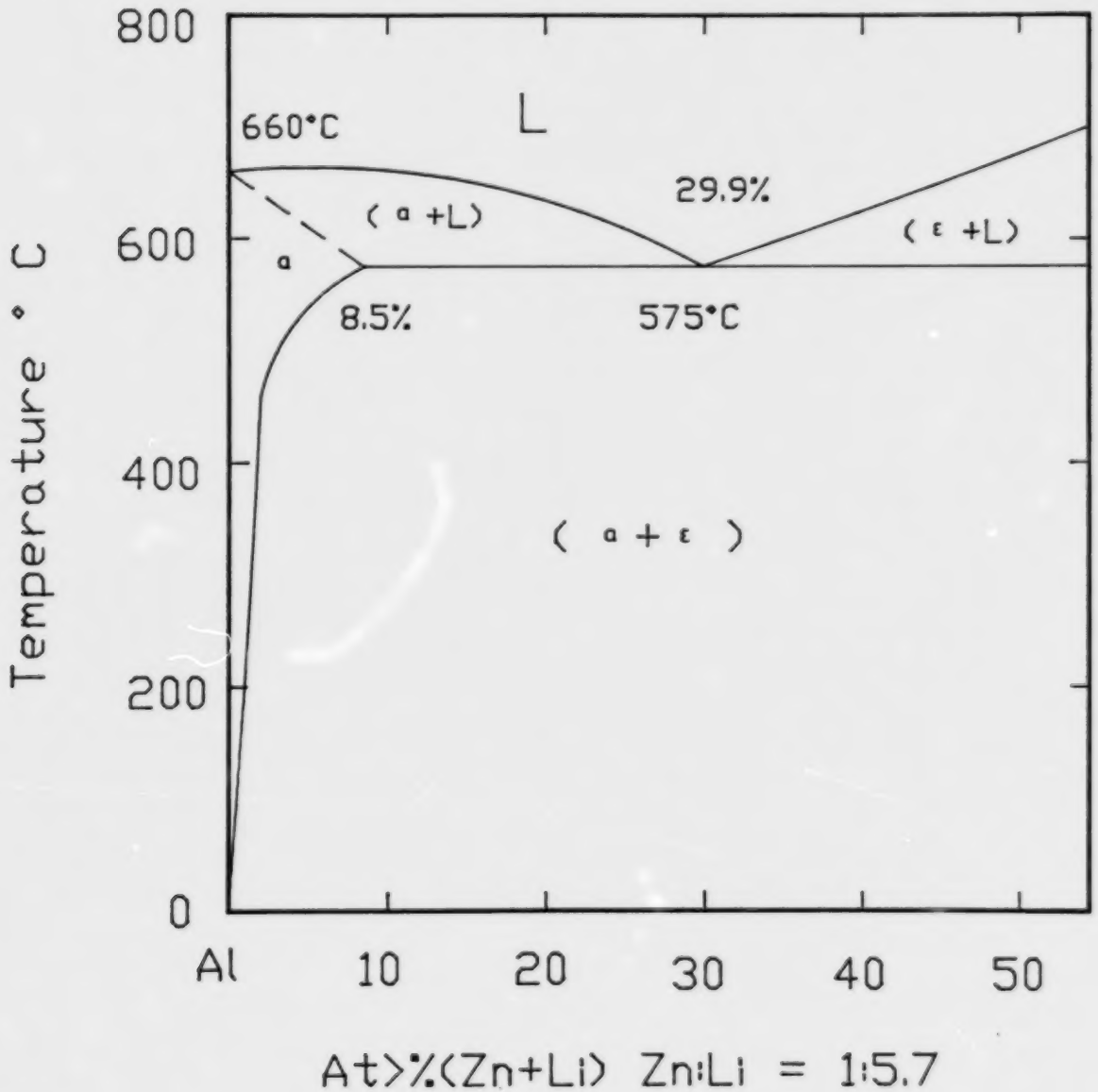

800
600
400
200
0
Temperature ° C
660°C
L
29.9%
(α +L)
(ε +L)
α
8.5%
575°C
(α + ε)
Al
10
20
30
40
50
At>%(Zn+Li) Zn:Li = 1:5.7

FIG. 9

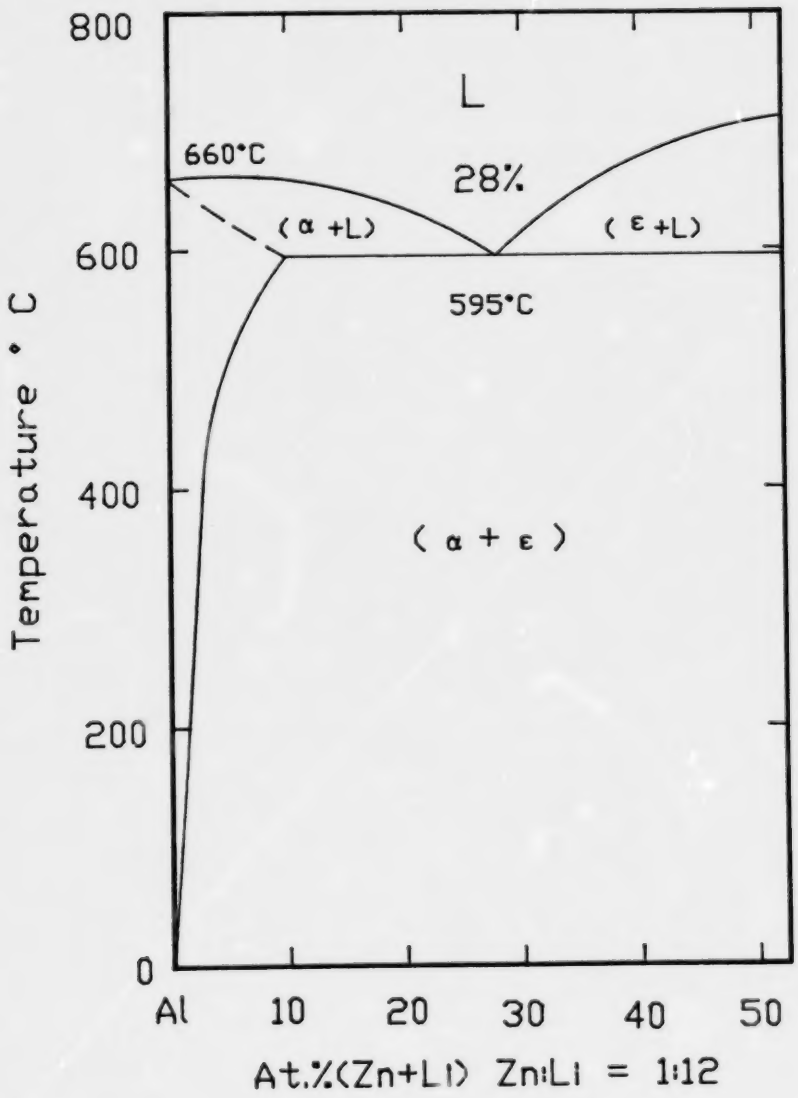

800
600
400
200
0
Temperature • C
L
660°C
28%
(α +L)
(ε +L)
595°C
(α + ε)
Al
10
20
30
40
50
At.%(Zn+Li) Zn:Li = 1:12

FIG. 10

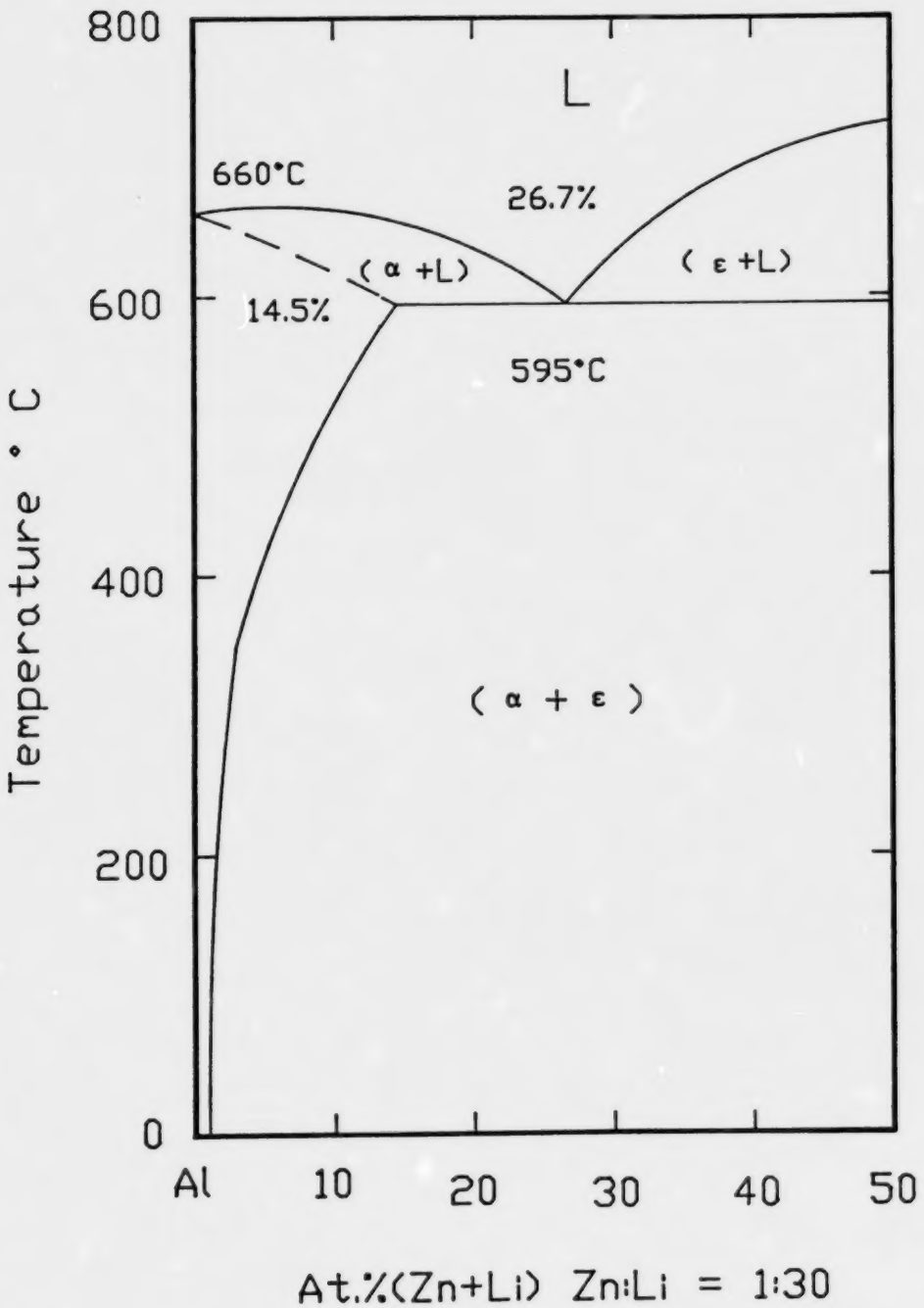

800
600
400
200
0
L
660°C
26.7%
(α +L)
(ε +L)
14.5%
595°C
(α + ε)
Temperature ° C
Al
10
20
30
40
50
At.%(Zn+Li) Zn:Li = 1:30

FIG. 11

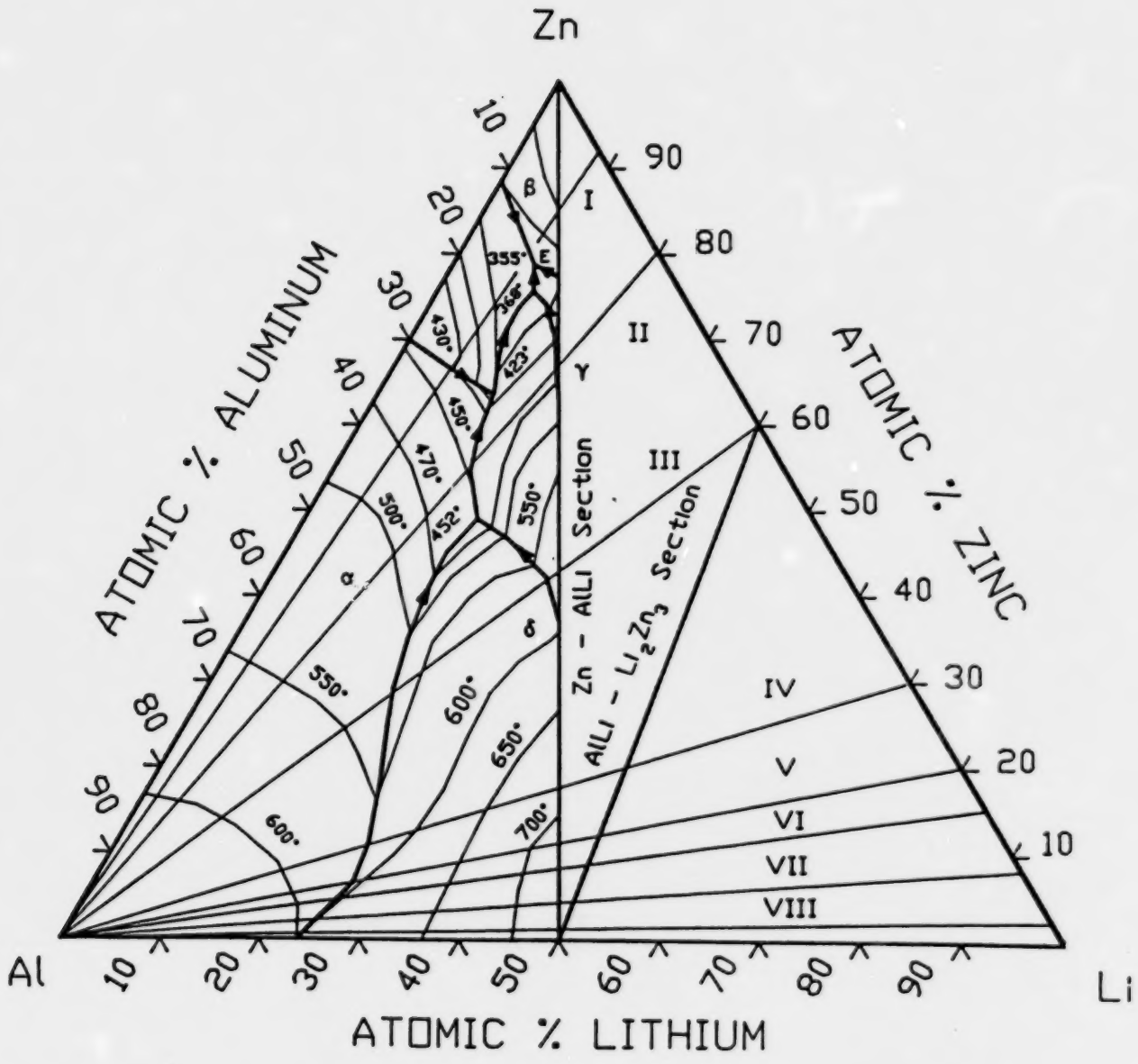

Zn
ATOMIC % ALUMINUM
ATOMIC % ZINC
ATOMIC % LITHIUM
Al
Li
Zn - AlLi Section
AlLi - Li2Zn3 Section
I
II
III
IV
V
VI
VII
VIII
α
β
γ
δ
ε
355°
365°
430°
423°
450°
470°
500°
452°
550°
600°
650°
700°

FIG.12

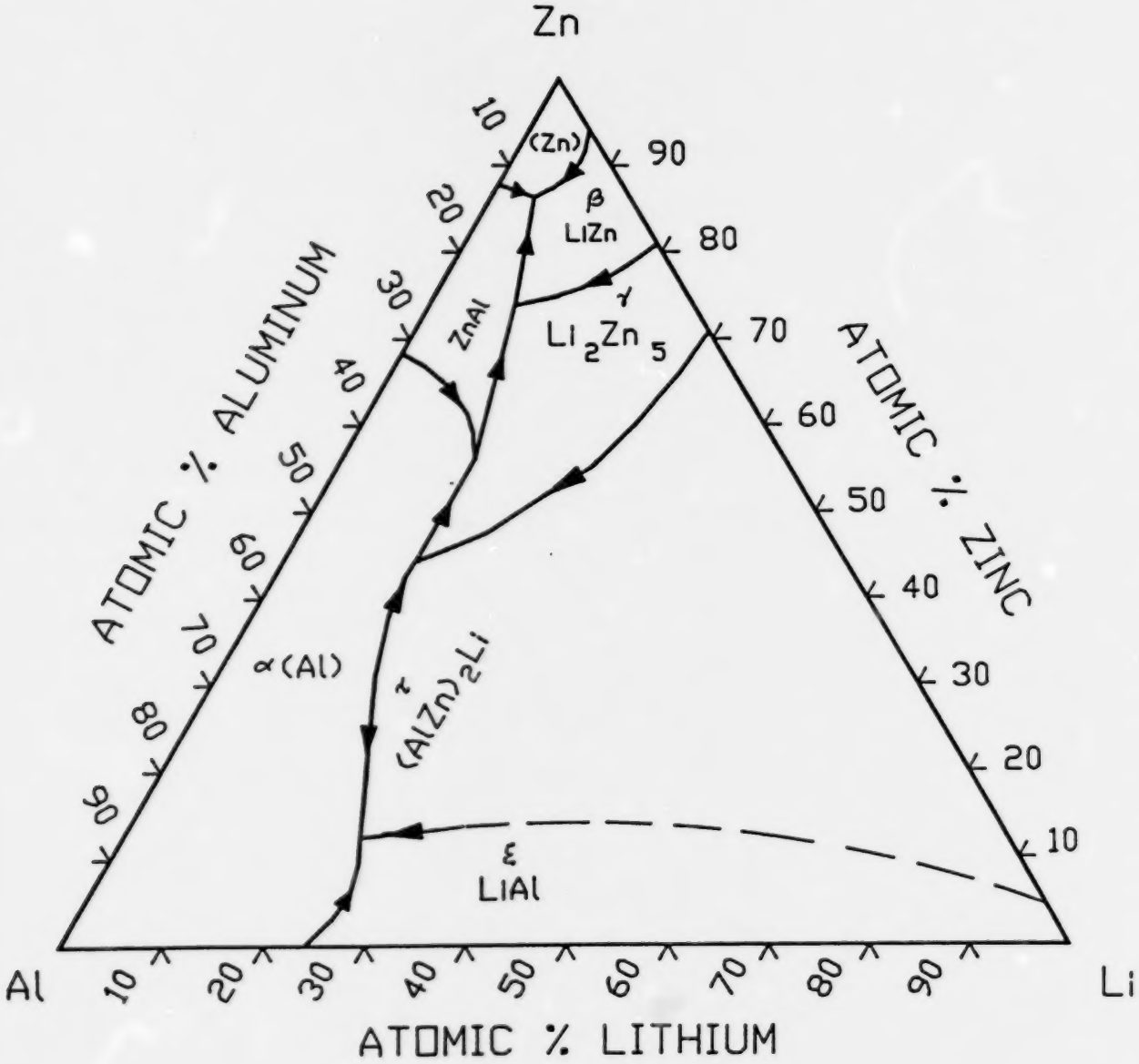

Zn
(Zn)
β
LiZn
γ
Li2Zn5
ZnAl
α(Al)
τ
(AlZn)2Li
ε
LiAl
Al
Li
ATOMIC % ALUMINUM
ATOMIC % ZINC
ATOMIC % LITHIUM
10
20
30
40
50
60
70
80
90

FIG. 13

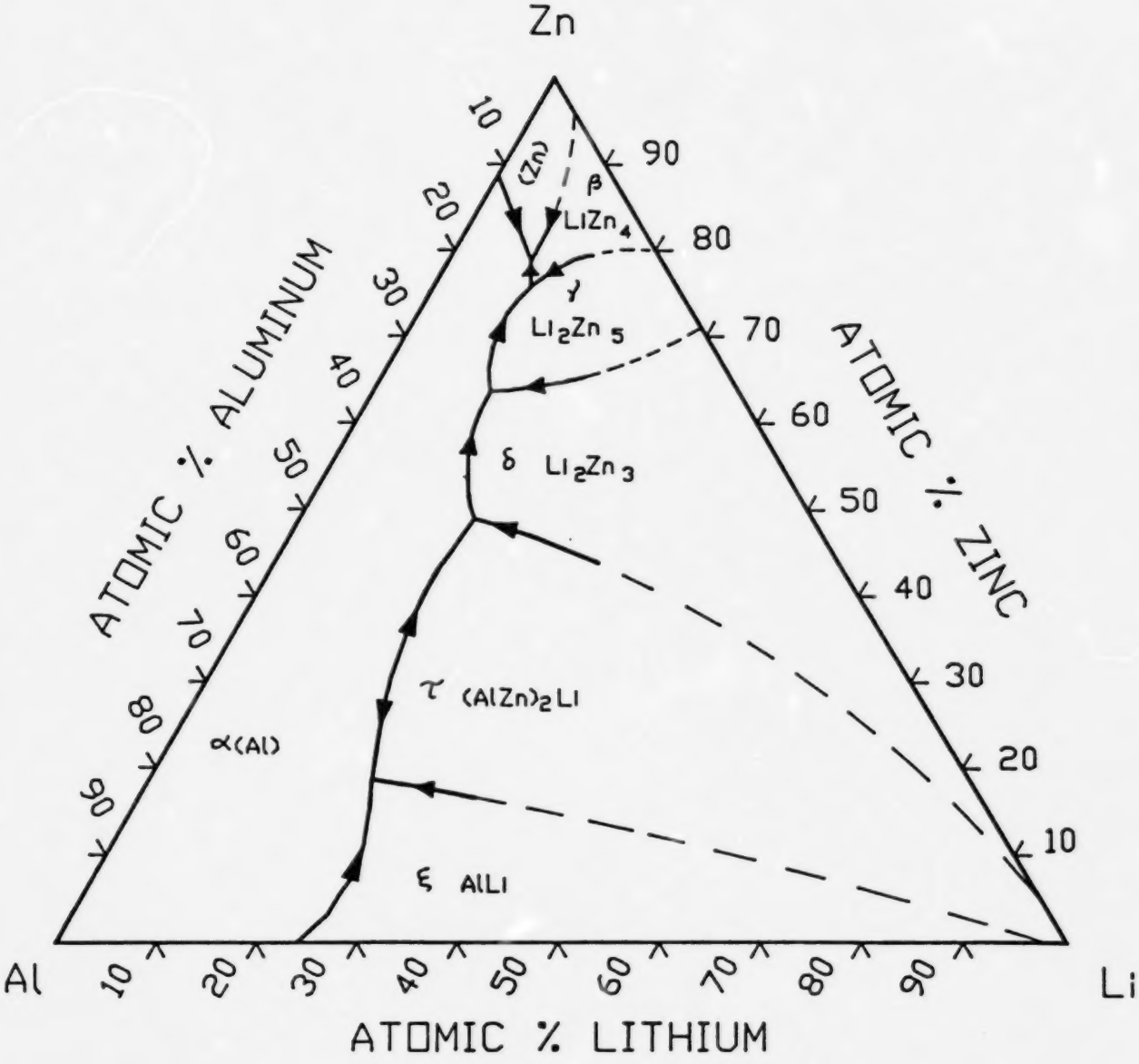

Zn
10
20
30
40
50
60
70
80
90
(Zn)
β
LiZn4
γ
Li2Zn5
δ Li2Zn3
τ (AlZn)2Li
α(Al)
ε AlLi
ATOMIC % ALUMINUM
ATOMIC % ZINC
Al
Li
ATOMIC % LITHIUM

FIG. 14

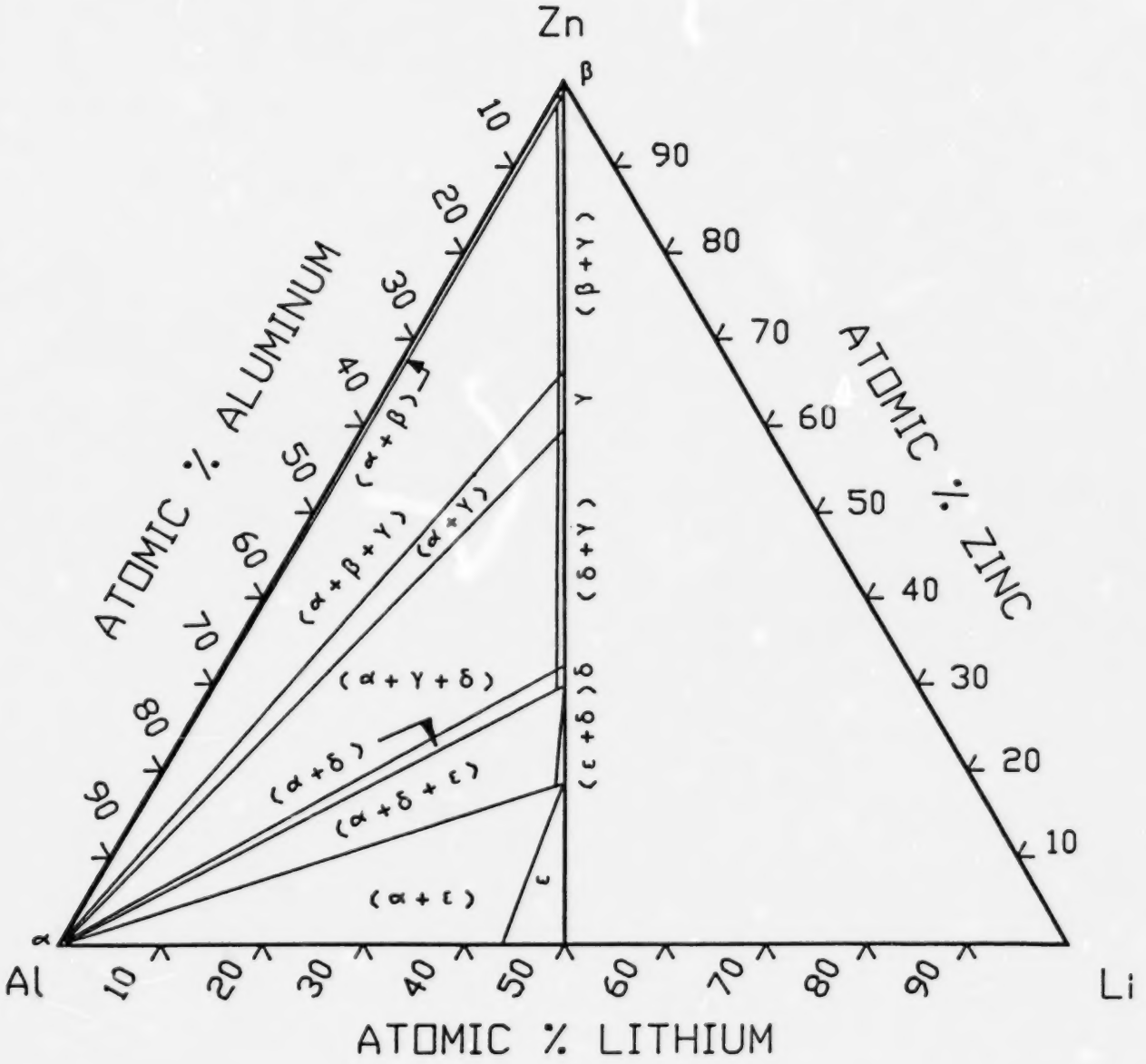

Zn
β
Al
α
Li
ATOMIC % ALUMINUM
ATOMIC % ZINC
ATOMIC % LITHIUM
10
20
30
40
50
60
70
80
90
(α+β)
(α+β+γ)
(α+γ)
(α+γ+δ)
(α+δ)
(α+δ+ε)
(α+ε)
(β+γ)
γ
(δ+γ)
δ
(ε+δ)
ε

FIG. 15

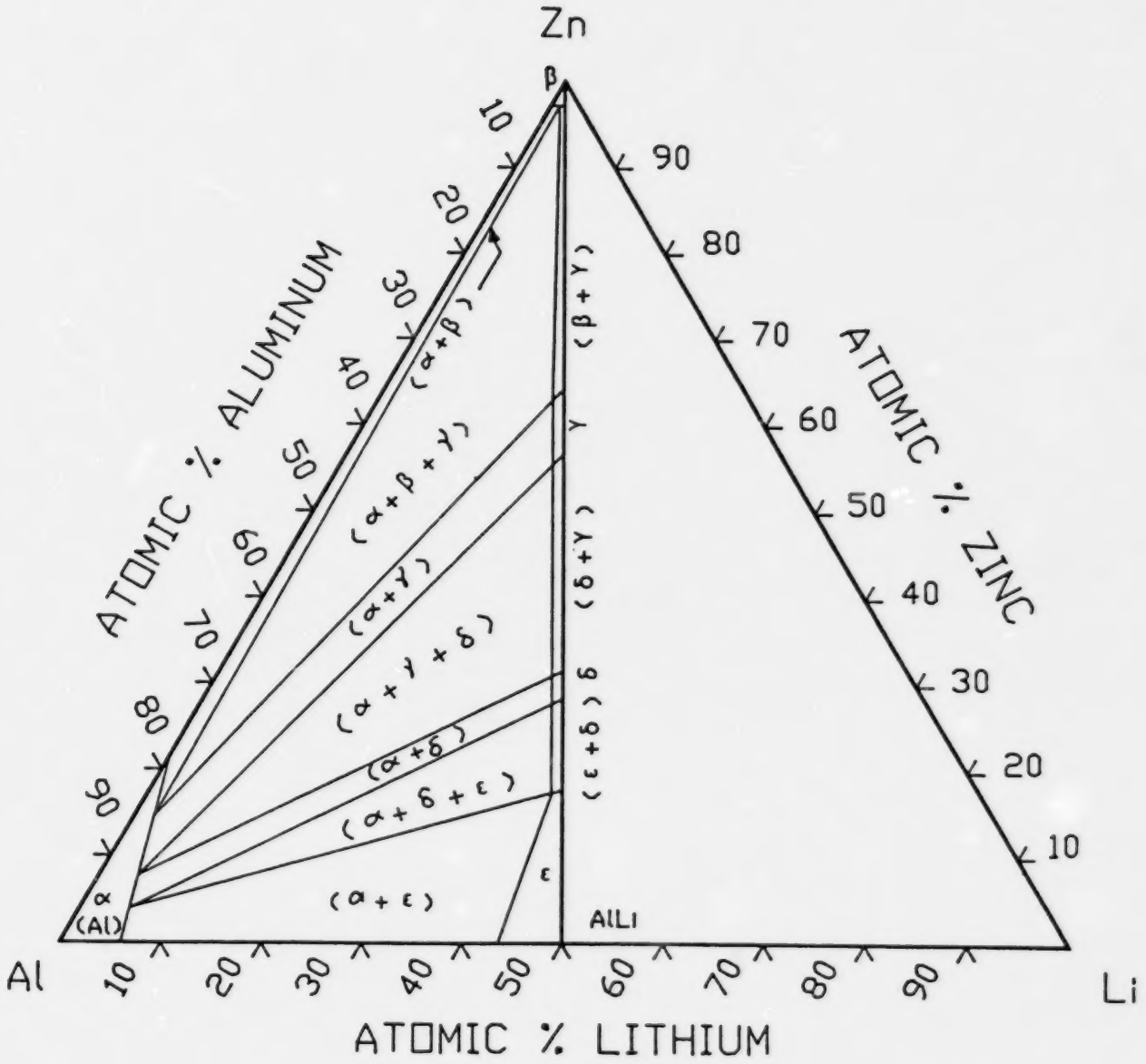

Zn
β
10
20
30
40
50
60
70
80
90
ATOMIC % ALUMINUM
(α+β)
(α+β+γ)
(α+γ)
(α+γ+δ)
(α+δ)
(α+δ+ε)
(α+ε)
α
(Al)
(β+γ)
γ
(δ+γ)
δ
(ε+δ)
ε
AlLi
90
80
70
60
50
40
30
20
10
ATOMIC % ZINC
Al
10
20
30
40
50
60
70
80
90
Li
ATOMIC % LITHIUM

FIG. 16

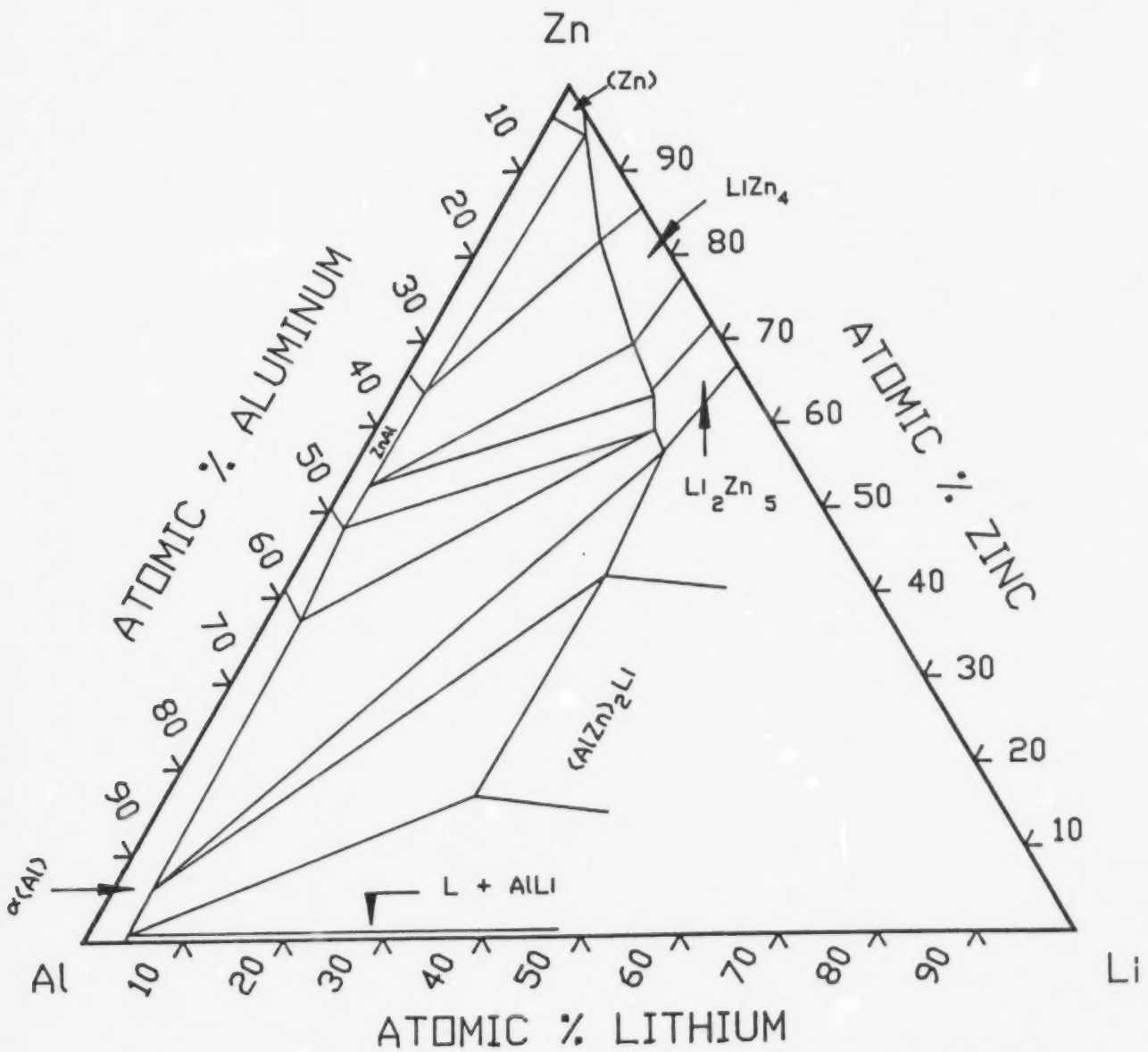

Zn
(Zn)
LiZn4
Li2Zn5
(AlZn)2Li
L + AlLi
α(Al)
Al
Li
ATOMIC % ALUMINUM
ATOMIC % ZINC
ATOMIC % LITHIUM
10
20
30
40
50
60
70
80
90

FIG. 17

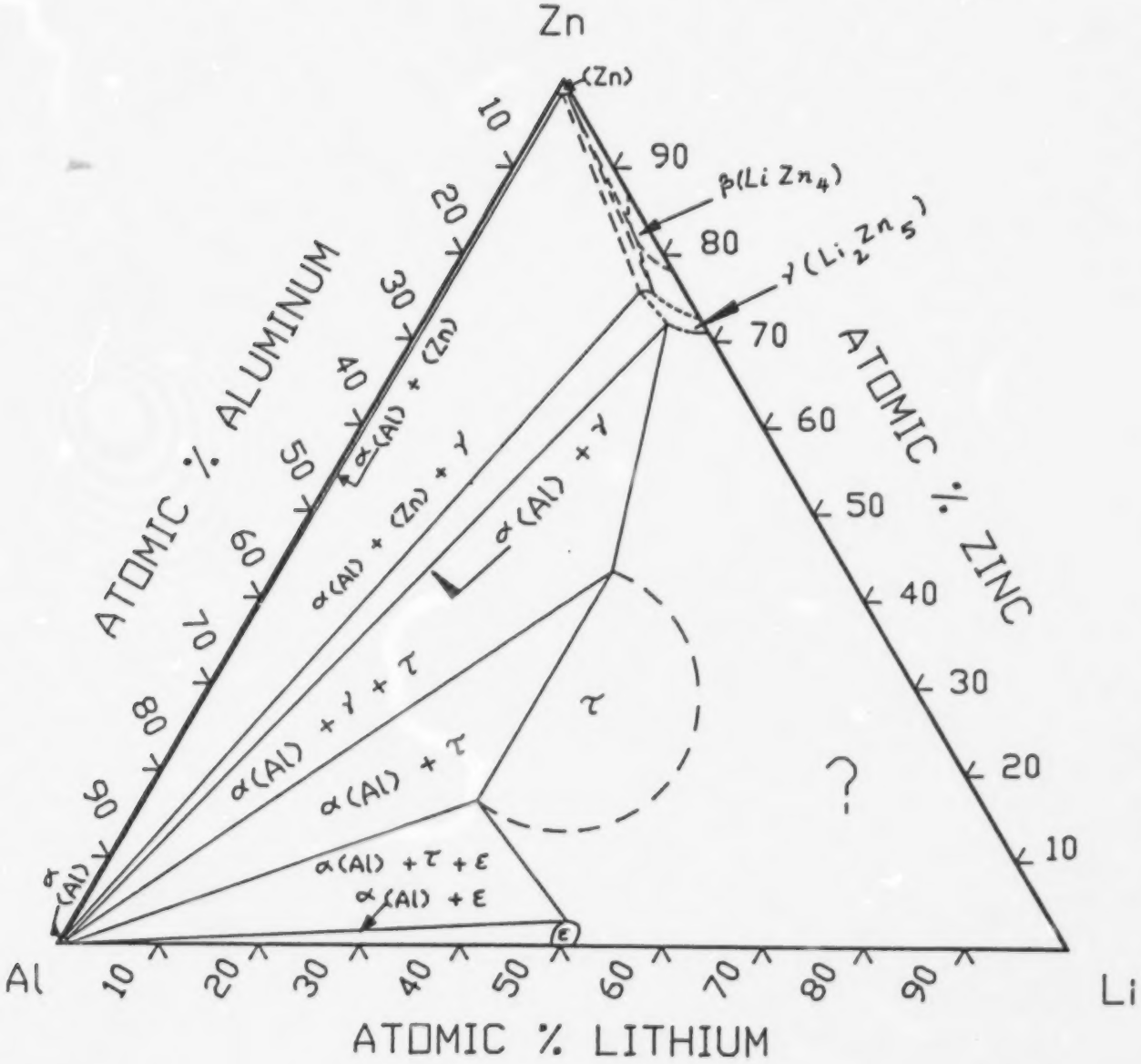

Zn
(Zn)
β(Li Zn4)
γ(Li2Zn5)
ATOMIC % ALUMINUM
ATOMIC % ZINC
α(Al) + (Zn)
α(Al) + (Zn) + γ
α(Al) + γ
α(Al) + γ + τ
α(Al) + τ
α(Al) + τ + ε
α(Al) + ε
τ
?
α(Al)
ε
Al
Li
ATOMIC % LITHIUM

FIG. 18

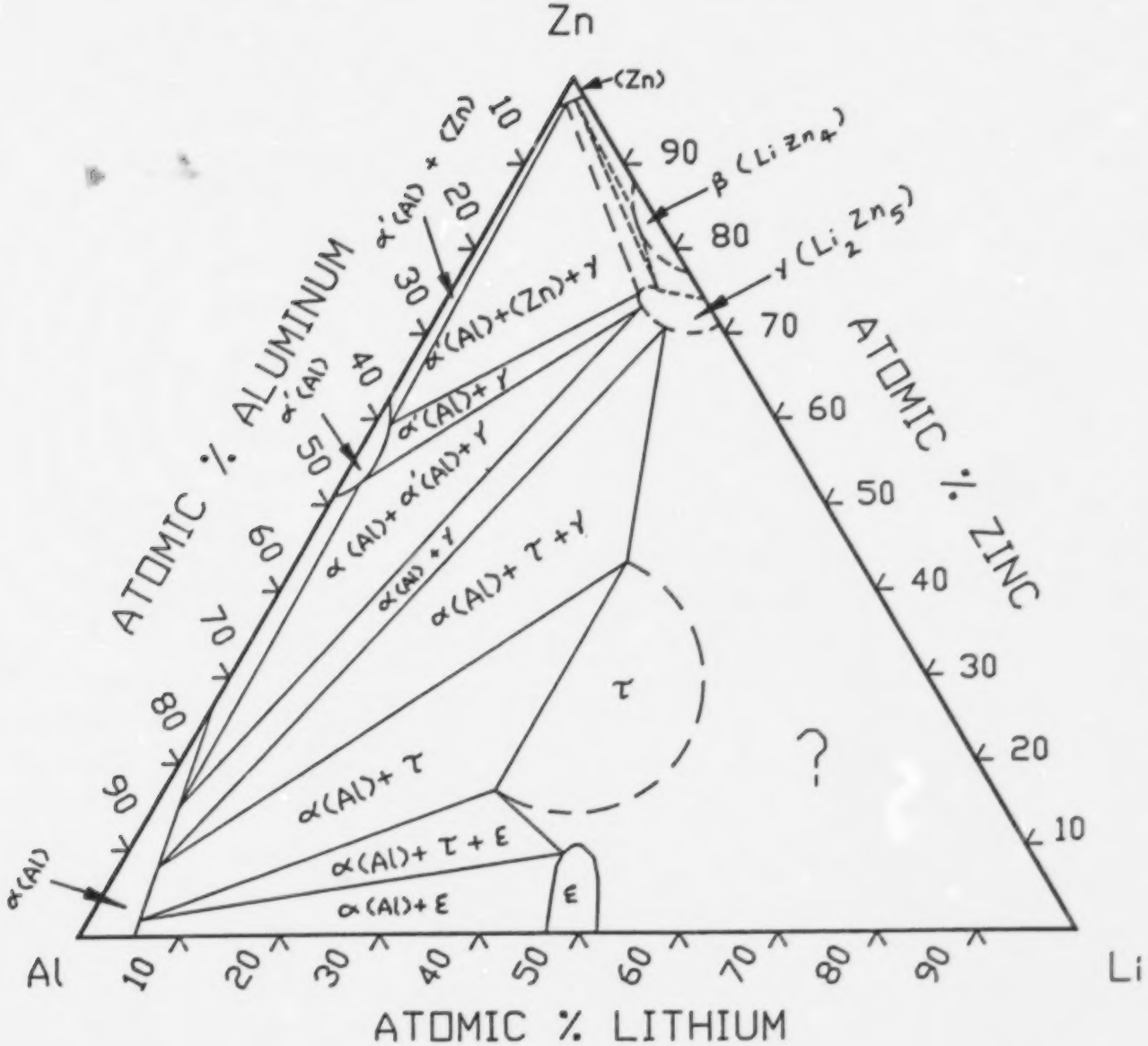
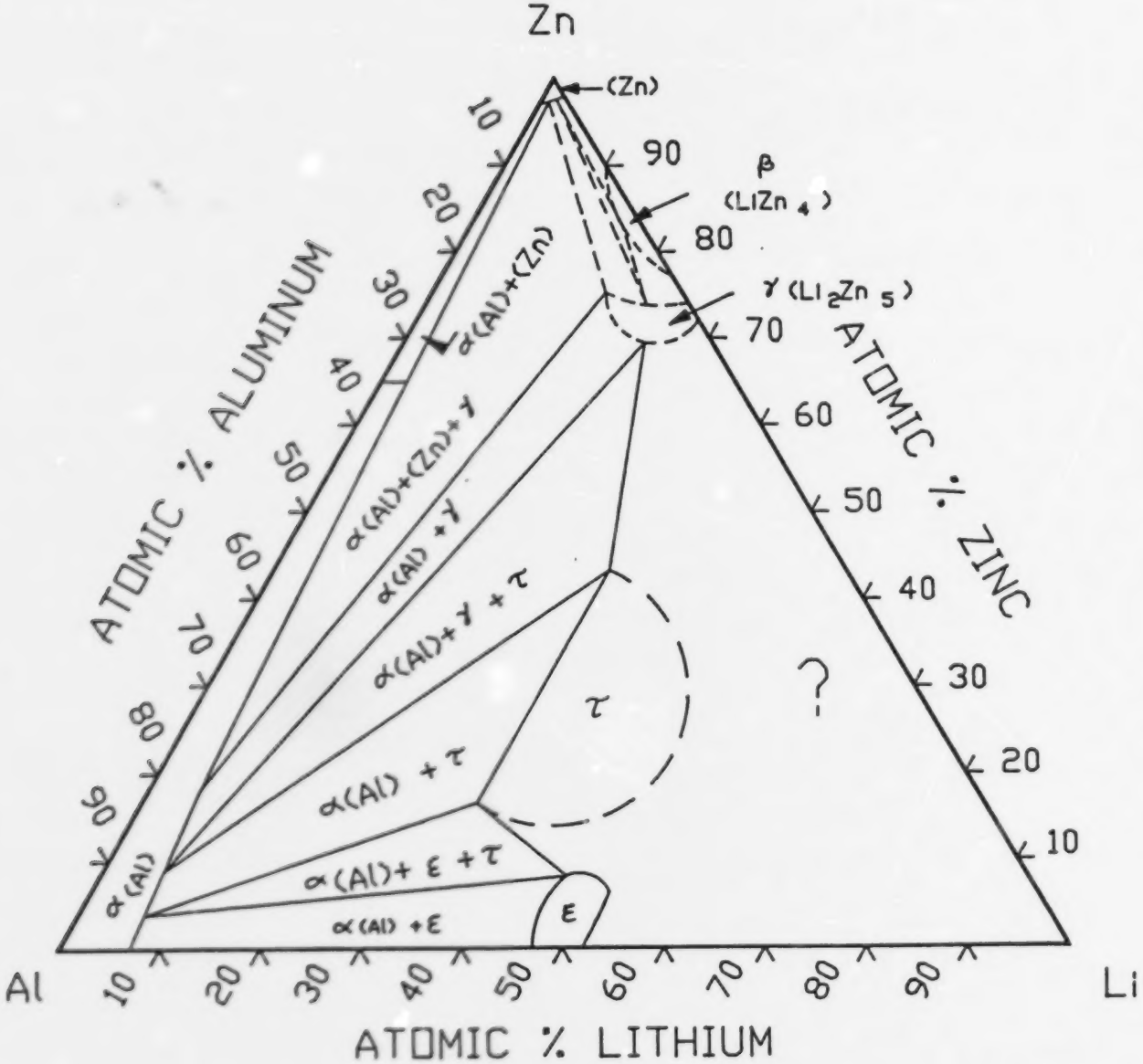

Zn
(Zn)
β (Li Zn4)
γ (Li2 Zn5)
α'(Al) + (Zn)
α'(Al)
α(Al)+(Zn)+γ
α'(Al)+γ
α(Al)+α'(Al)+γ
α(Al)+γ
α(Al)+τ+γ
τ
?
α(Al)+τ
α(Al)+τ+ε
α(Al)+ε
ε
α(Al)
ATOMIC % ALUMINUM
ATOMIC % ZINC
Al
Li
ATOMIC % LITHIUM
10
20
30
40
50
60
70
80
90

FIG. 19


Zn
(Zn)
β
(LiZn 4)
γ (Li2Zn 5)
α(Al)+(Zn)
α(Al)+(Zn)+γ
α(Al)+γ
α(Al)+γ+τ
α(Al)+τ
α(Al)+ε+τ
α(Al)+ε
α(Al)
τ
?
ε
ATOMIC % ALUMINUM
ATOMIC % ZINC
Al
Li
ATOMIC % LITHIUM

Aluminum-Lithium-X Ternary Systems

Part VI

The Al-Li-X (Where X = Ag, As, P, B, Cd, Ge, Fe, Ga, H, In, N, Pb, S, Sb, and Sn) Systems

Al-Li-X Systems

Introduction:

Besides the ternary systems Al-Li-Mg, Al-Li-Mn, Al-Li-Si, Al-Li-Cu and Al-Li-Zn, which are being published separately by the authors, several other Al-Li-X (where X = Ag, As, P, B, Cd, Ge, Fe, Ga, H, In, N, Pb, S, Sb and Sn) ternary systems were also looked into to present a more complete review on Al-Li-X ternary systems.

Whereas the Al-Li-X systems with X = Mg, Mn, Si, Cu and Zn have been investigated primarily with a viewpoint of developing new structural materials, other Al-Li-X systems have been studied to develop electrode material.

Al-Li-Ag System:

The only study available on Al-Li-Ag system is by [68PAU] as also summarized by [84JON], who have reported the presence of a ternary phase Li_2AgAl. This phase is stable only in a dry atmosphere and decomposes within a few hours in moist air. The composition and the crystallographic data for this compound are listed in Table 1.

Al-Li-As and Al-Li-P Systems:

The only information available on these two systems is the reported occurrence of the ternary phases As_2Li_3Al and P_2Li_3Al [52JUZ] with the crystallographic and compositional details as given in Table 1. It is considered doubtful that these compounds are in equilibrium with aluminum.

Al-Li-B System:

The only information available on this system is due to [83ITO and 81 HIG] who have studied the charge density distribution and crystal structure of the ternary compound $LiAlB_{14}$ (Table 1).

Al-Li-Cd System:

No relevant information pertaining to this system has been found.

Al-Li-Ge System:

[52BOO, 54BOO] and [76SCH] have shown the existence of a ternary compound GeLiAl in this system. Crystallographic and compositional details for this compound are listed in Table 1. Lithium compounds being good nucleating agents for germanium are claimed to modify Al-Ge alloys [54BOO].

Al-Li-Fe System:

The interest in this system has been limited to its applications in high specific energy Li battery anodes [83DOE]. No ternary compounds have been identified in this system.

Al-Li-Ga System:

No relevant information pertaining to this system has been found.

Al-Li-H System:

[53HEY] has reported a ternary compound H_4LiAl in this system with heat of formation of the order of 110-120 kJ/mole [71SEM]. [73TEM] has shown by neutron scattering that this phase is analogous to H_4NaAl.

Al-Li-In System:

[75YAH] have studied the composition dependence of the lattice constant for this system and have identified a ternary compound Li_2Al In with details as given in Table 1. This compound which shows a blue metallic luster is sensitive to moist air, but is found stable in vacuum or in paraffin-oil. Their results indicate that the Li $Al_{1-x}In_x$ system forms a solid solution over the entire range of composition and follows Vegard's law. They have also shown that the structure of Li_2Al In is B32A-type lattice in which Li atoms make one diamond type sublattice with Al and In atoms being arranged at random on the other diamond type sublattice sites.

Al-Li-N System:

[46JUZ, 48JUZ] have reported the presence of a ternary compound Li_3N_2Al for this system. This compound, as indicated in Table 1, forms as a superstructure of CaF_2 with 8 unit cells of a crystal of space group Fm3m. It is not known whether this compound is formed in aluminum-rich alloys.

Al-Li-Pb System:

[36KOM] have reported a quasibinary section Pb-LiAl. Upon centrifuging the alloys on this quasibinary section, the LiAl compound decomposes to form PbLi and aluminum.

Al-Li-S System:

[79HEL] has reported the presence of a ternary compound $LiAlS_2$ in this system. This compound has an orthorhombic structure as per details given in Table 1.

Al-Li-Sb System:

[83LUE], using thermodynamic data, have attempted to determine the stability ranges of the 3-phase regions and to evaluate the ternary phase diagram for this system. No intermediate ternary phase is found to exist. A comparison of the thermodynamic data from their electrochemical experiments with that calculated from the thermodynamic data of the corresponding binary systems reported in the literature shows good

agreement. Also, earlier attempts of [52JUZ] to prepare a ternary compound Li_3AlSb_2 similar to Li_3AlAs_2 and Li_3AlP_2 were unsuccessful.

Al-Li-Sn System:

In an attempt to develop electrode materials for applications in high specific energy Li-S battery systems, [81KIS] have studied the effect of the additions of a third element M (M = Ge, Sn, In, Ag) on the intermetallic compound AlLi at the quasi-binary composition $Li_{50}Al_{50-x}M_x$ using x-ray diffraction and density measurements. [81KIS] have identified the presence of some unknown ternary compounds having f.c.c. structures of the NaTl type in germanium and tin-doped Al-Li alloys (Table 1). They have also shown that the solubilities of germanium and tin were less than x=1, while indium and silver showed solubilities of at least x=5.

Cited References:

36KOM: Komovsky, G. "Use of Centrifuge for the Study of Alloys", Metallurg., 11, No. 12, pp. 120-22; Physik Z. Sowjet union, 10, pp. 840-42 (1936).

46JUZ: Juza, R. and Hund, F., "The Crystal Structures of LiMgN, LiZnN, Li_3AlN_2 and Ni_3GaN_2", Naturwiss. 33, p. 121-22 (1946).

48JUZ: Juza, R. and Hund, F., "Metal Amides and Metal Nitrides. XVII. The Ternary Nitrides Li_3AlN_2 and Li_3GaN_2", Z. Anorg. Chem. 257, pp. 13-25. (1948).

52BOO: Boom, E.A., "New Phases in the System Al-Na-Ge and Al-Ge-Li", Dok. Akad. Nauk. S.S.S.R., 84, pp. 697-99 (1952).

52JUZ: Juza, R. and Schulz, W., "Preparation and Properties of Li_3AlP_2 and Li_3AlAs_2", Z. Anorg. u. Allgem. Chem., 269, pp. 1-12 (1952).

53HEY: Heyrowsky, J., "Oscillographic Depolarization Effect of Al-Ion", Chem. Listy, 47, pp. 1762-67 (1953).

54BOO: Boom, E.A., "Reaction of Germanium with Chemical Elements", Khim. Redkikh Elementov, Akad. Nauk. S.S.S.R., 1, pp. 121-30 (1954).

68PAU: Pauly, H., Weiss, A. and Witte, H., "Lithium-E-X (E=copper, silver, gold; X = aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, antimony and bismuth)", Z. Metallkde. 59, pp. 47-58 (1968).

71SEM: Semenchenko, K.N., Ilina, T.S. and Surov, V.I., "Enthalpy of Lithium Tetrahydroaluminate Formation", Z. Neorg. Khim., 16(6), pp. 1516-20 (1971).

73TEM: Temme, F.P. and Waddington, T.C., "Librational Motion in Sodium and Lithium-Aluminum Hydrides, studied by Inelastic Neutron Scattering", J. Chem. Soc. Faraday Trans., II, 69(6), pp. 783-90 (1973).

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81KIS: Kishio, K. and Brittain, J.O. "Phase Stability of Doped β-LiAl", Materials Science and Engineering, 49, pp. P1-P6 (1981).

81HIG: Higashi, I., "The Crystal Structure of $LiAlB_{14}$", J. Less-Common Met., 82, pp. 317-23 (1981).

83DOE: Doench, J.P. and Huggins, R.A., "Ternary Alloys as Anodes in Lithium Systems", Proc. Electrochem. Soc. 83(7), pp. 115-22 (1983).

83ITO: Ito, T. and Higashi, I., "The Charge Density Distribution in $LiAlB_{14}$", Acta Cryst., B39, pp. 239-43 (1983).

83LUE: Luedecke, C.M., Doeuch, J.P. and Huggins, R.A., "Thermodynamic Studies of the Lithium - Aluminum-Antimony System", Proc. Electrochem. Soc., 83(7), pp. 105-14 (1983).

84JON: Jonsson, S., "Ag-Al-Li System", Private Communication (1984).

Table 1: Phases, their composition and crystallographic data in Al-Li-X Ternary Systems.

Phase/ Temp °C	Approximate Composition wt% Al	Li	X	Pearson Symbol or Crystallographic Structure/Space Group	Prototype	Lattice Parameters in nm a	b	c	Reference	Comments
As_2Li_3Al	13.6%	10.6%	Bal. As	oI96/Ibca (96 atoms per unit cell)	$AlAs_2Li_3$	1.1865	1.1981	1.2114	[52JUZ]	These phases may not be in equilibrium with Aluminium
P_2Li_3Al	24.5%	19.1%	Bal. P.	oI96/Ibca (96 atoms per unit cell)	$AlAs_2Li_3$	1.1471	1.1610	1.1731		
Li_2AgAl	18.1%	9.4%	Bal. Ag.	cF16/f $\bar{4}3m$ (16 atoms per unit cell)	NaTl	0.635	-	-	[68PAU] [81KIS]	This phase is not yet ascertained to be in equilibrium with Aluminium
REMARKS: $Ag_{(x)}Al_{(50-x)}Li_{50}$, x = 0 - 5.0 at room temperature										
Li_2AlIn	-	-	-	cF16/$Fd\bar{3}m$ (16 atoms per unit cell)	NaTl	66.1 ± 0.08			[75YAH] [81KIS]	Li $Al_{1-x}In_x$ System makes solid solution in the whole range of composition and follows Vegard's Law
REMARKS: $Al_{(50-x)}In_{(x)}Li_{50}$, x = 0 - 5.0										
GeLiAl	25.3%	6.5%	Bal. Ge	cF12/$Fm\bar{3}m$ (12 atoms per unit cell)	$NaSi_6Al$/ AlLiSi	0.5989	-	-	[76SCH]	
Al-Ge-Li	-	-	-	cF16/$Fd\bar{3}m$	NaTl	0.6337	-	-	[81KIS]	
REMARKS: $Al_{(50-x)}Ge_{(x)}Li_{50}$, x = 0 - 6.0										

Table 1: Phases, their composition and crystallographic data in Al-Li-X Ternary Systems.

Phase/ Temp °C	Approximate Composition wt% Al	Li	X	Pearson Symbol or Crystallographic Structure/Space Group	Prototype	Lattice Parameters in nm a	b	c	Reference	Comments
$AlLi_3N_2$	29.2%	30.3%	Bal. N.	cI96/$Ia\bar{3}$ (96 atoms per unit cell)	$AlLi_3N_2$	0.9461	-	-	[46JUZ, 48JUZ]	
$AlLiH_4$	71.2%	18.3%	Bal.H.	"	H_4NaAl	"	"	"	[71SEM, 73TEM]	
$AlLiS_2$	"	"	"	oP16/$Pna2_1$	MnN_2Si	0.6484	0.7875	0.6188	[79HEL]	
$AlB_{14}Li$	15.0%	3.5%	Bal.B.	oI16/Imma	B_7Mg	0.5846	1.0354	0.81429	[81HIG]	
Al-Li-Sn	"	"	"	cF16/$Fd\bar{3}m$	NaTl	0.6325	-	"	[81KIS]	

REMARKS: $Al_{(50-x)}Li_{50}Sn_{(x)}$ x = 0 - 6.0

Aluminum - Lithium - X Ternary Systems

Part VII

An Experimental Technique for the Rapid Determination of Binary and Ternary Phase Diagrams

Binary Systems - Al-Mg Diagram

INTRODUCTION

The importance of phase diagrams is immense in all aspects of material development. The conventional method of casting, heat treatment and subsequent analysis of literally hundreds of samples of varying composition might take years of tedious work to completely determine the phase diagram for even simple systems. The technique of using solid state diffusion couples comprising two pure metals for the determination of binary phase diagrams has found limited use since the solid state diffusion is relatively slow, and not all phases appear due to differences in diffusion rates.[1] A new method of phase diagram determination involving liquid diffusion couples which allows rapid determination of phase diagrams and any number of isothermal sections has been developed and reported in this investigation. In its simplest form, this method consists of producing a diffusion couple with the concentration of elements varying continuously across the portion of the diagram being intestigated, heat treating and then performing microscopic and micro-chemical analysis on the couple to identify phases. This method has been found to apply equally well for the determination of ternary as well as binary phase diagrams. The couple contains all phases and all phase fields in the composition range and therefore there is little ambiquity in identification of phases.

In this communication we describe the new experimental technique used to determine binary phase diagrams and report some of the results

that we have obtained to clarify the confusion concerning the occurrence of various phases in the Al-Mg binary system in the composition range 35 wt. % to 50 wt. % Mg. The presence of R phase at approximately 42 at. % Mg has been reported by several researchers[2-8]. However, the temperature range for the existence of this phase remains in doubt, for example, Murray[6] has reported that the R phase forms by the peritectoid reaction of Al_3Mg_2 (β) and $Al_{12}Mg_{17}$ (γ) phase at 370 ± 5°C, and that it transforms back to (β + γ) below approximately 320°C. Conversly Schürmann and Voss[6,7] have reported this phase (designated ε by them) to be formed via the following two reactions:

$$\text{Liquid (40.8 at. \% Mg)} \overset{448°C}{\rightleftharpoons} \beta \text{ (39.5 at. \% Mg)} + \varepsilon \text{ (42.5 at. \% Mg)}$$

and

$$\text{Liquid (42.5 at. \% Mg)} + \zeta \text{ (46.4 at. \% Mg)} \overset{450°C}{\rightleftharpoons} \varepsilon \text{ (44.6 at. \% Mg)}$$

where the ζ phase is AlMg. Schürmann and Voss[7,8] reported that the ζ phase forms between the composition range of 46.4 at. % Mg and 48.1 at. % Mg and a temperature range of 410 and 450°C via the following two peritectic reactions:

$$\text{Liquid (42.5 at. \% Mg)} + \zeta \text{ (46.4 at. \% Mg)} \overset{450°C}{\rightleftharpoons} \varepsilon \text{ (44.6 at. \% Mg)}$$

a n d

$$\text{Liquid (44.5 at. \% Mg)} + \gamma \text{ (50.6 at. \% Mg)} \overset{450°C}{\rightleftharpoons} \zeta \text{ (48.1 at. \% Mg)}$$

This phase ζ(AlMg) has not been reported by any other researcher.

Principle of Liquid Diffusion Couple Technique:

Binary Systems: The principle of the liquid-diffusion couple technique for determining the phase diagrams can be understood by considering the binary system AB, shown schematically in Fig. 1. Consider a liquid diffusion couple made by heating pieces of pure elements A and B placed face to face at a temperature about 50°C above the melting temperature of the higher melting metal. Typical piece sizes would be 9mm diameter and 12.5mm length. Upon melting, there may be convective mixing between the two metals. However, the mode of transport is not important as long as a continuous concentration gradient is produced as shown in Fig. 2a. Assuming that the solidification rate is fairly rapid, solidification of an alloy of composition X_1 in the couple (Fig. 1) will yield cored α plus the eutectic, E_1. In fact, every composition from pure A to E_1 will give cored α plus E_1. Similarly, all compositions from E_1 to X_2 will give cored β plus E_1, compositions from X_2 to E_2 will give cored β plus E_2, and compositions from E_2 to B will give cored γ plus E_2. Therefore, the couple, in the as solidified state, should give the alternating phase fields as indicated in Fig. 2a. From this couple, liquid-solid reactions, such as eutectics and the number of phases present, may be identified.

Upon heat treatment at some temperature, T, below T_2, a continuous concentration gradient will result (Fig. 2b). There will be little mass transport along the length of the couple since solid state diffusion is slow. However, local equilibrium will be obtained. Consequently, equilibrium solid solubilities result, coring is eliminated, and equilibrium

phase relations, as depicted in Fig. 2b, are obtained. Microanalysis can be used to establish phase composition. In principle, a single couple could be heat treated and analyzed at various temperatures to yield a complete phase diagram. However, for more precise determination of a particular region of a phase diagram, two alloys encompassing the region of interst could be made, heat treated and analyzed.

Experimental Procedure:

Preparation of Diffusion Couples:

99.999% pure aluminum ingots and 99.9% pure magnesium rods were used in this investigation. The size chosen as standard for the diffusion couple was 9mm diameter. This size was large enough to be handled conviniently and also had a cross section large enough for metallographic examination.

The molds were constructed from a 25mm diameter graphite rod with a 9mm diameter hole drilled centrally. The two halves of the couple were made either from pure Al and Mg metals, or from 30% Mg - Al and 70% Mg - Al alloys, or from 35% Mg - Al and 47% Mg - Al alloys depending on the relevant section of the Al - Mg being investigated. Each half of the couple was machined to 9mm diameter and 12.5mm long to form a Boltzman - Matano type diffusion couple of 25mm in length (Fig. 3). After the end pieces of the couple had been placed in the mold, graphite plugs were placed at the open ends and the whole assembly was compressed in a small steel jig. This provided a token air seal, and served to press the two pieces of the couple together. The couple was then placed vertically in a furnace for 20 to 30 minutes at a temperature about 50°C above the liquidus of the higher melting

point material. The couple was removed from the furnace and allowed to solidify in air. It was then heat treated at a given temperature between 280°C and 435°C for times up to 3 weeks and water quenched to obtain the equilibrium phases in the Al - Mg binary system.

All specimens were metallographically polished to 0.05 μm alumina powder and chemically etched. A two step chemical etching was used. The polished specimen was immersed in a 10% sodium hydroxide solution for about 30 seconds, rinsed with water, then etched in a solution of 75% ethylene glycol + 24% H_2O + 1% HNO_3 for about 30 seconds. Micro-chemical analysis of individual phases was done on a JEOL SEM Model JXA-840 scanning microanalyzer equipped with a Tracor Northern energy dispersive system.

Results and Discussion:

Metallographic examination of the as-cast aluminum magnesium couple showed the same number of phases and phase reactions as reported by Hansen[9] and as also found in a recent assessment of the Al - Mg binary system by Murray[6]. Hence the phases were tentatively identified as α, β, γ and δ in order of their appearance from the aluminum-rich end to the magnesium end of the couple.

The general arrangement of phase fields as observed in the couple from the aluminum end to the Magnesium end was as schematically shown in Fig. 4 and is the same as reported by Hansen[9] and Murray[6].

Two eutectics L → β + γ and L → γ + δ, as reported in Murray's assessment were evident in this couple (Fig. 5c and 5f). The L → α + β eutectic contained too little α to be distinguished. The (α + β), pure β,

(β + γ), pure γ and (γ + δ) phase regions are shown in figures 5a - f. It should be noted from these figures that since aluminum (melting point 660°C) and magnesium (melting point 650°C) have similar melting points, convection is not expected to be significant to destroy the concentration gradient and therefore the phase field boundaries are seen as almost straight parallel lines running across the couple.

After observation of the as cast couples, several diffusion couples were heat-treated at temperatures between 280°C and 435°C for time up to 3 weeks and water quenched to determine if the R and ζ phases exist and if so, the temperature range over which they are present. As pointed out earlier, Murray's assessment of Al - Mg binary system suggests that R phase has an approximate composition of 42 at. % (39.48 wt. %) Mg with a range of about ± 0.3 at. % and forms by the peritectoid reaction of β and γ at 370 ± 5°C transforming back to (β + γ) below approximately 320°C. Schürmann and co-workers[7,8], on the other hand report the formation of ε phase (equivalent to the R phase) through a peritectic reaction at 450°C with a composition range between 42.5 at. % and 44.6 at. % Mg and a temperature range between approximately 425° and 450°C. The results of the examination of various heat treated couples are summarized in Table I which show that the R phase forms (from the β + γ phase field) at 400 ± 5°C. However, whether the R phase transforms via a eutectoid transformation back to β + γ at a temperature below 305 ± 5°C is not established.

Figure 6a shows the photomicrograph of a diffusion couple comprising Al-30% Mg alloy and Al-70% Mg alloy annealed at 370 ± 5°C for one week and water quenched. The presence of β, (β + R), R and (R + γ) phase fields in place of the β and β + γ phase field in the as-cast couple can be clearly seen in this photomicrograph. Figure 6b shows the photomicrograph of the same sample which was further annealed at 280°C for 3 weeks and water quenched. It can be seen from this micrograph that the R phase, which was formed by annealing the couple at 370°C for one week, does not dissolve at the lower temperature of 280°C. However, the R phase did not form at 280°C by annealing an as-cast couple for as long a period as three weeks. Therefore the R phase does not precipitate from the β + γ phase field at 280°C nor does it dissolve at 280°C if it is already present (from formation at higher tempertures). It may be concluded that transformations involving the R phase are very sluggish.

It should also be noted from these micrographs that since it takes a longer time of etching to reveal the R phase, the γ phase has been over etched and appears black in contrast to the γ phase in Fig. 5c which appears light gray. The dark gray curved streaks around the cracks are developed as a result of long time annealing of the couples.

In order to identify the presence of the ζ phase reported by Schürmann and co-workers, a number of liquid diffusion couples with i) pure Al and pure Mg, ii) 30% Mg - Al alloy and 70% Mg alloy, and iii) 35% Mg - Al alloy and 47% Mg - Al alloy as the two halves of the couples were made. These couples were then heat treated at a number of temperatures between 410°C and 435°C for periods up to 2 weeks and subsequently water quenched. Also, one

of the couples with 35% Mg - Al alloy and 47% Mg - Al alloy as its two halves was diffused at 525°C for 30 minutes, furnace cooled to 435°C, kept at 435°C for 48 hours and then quenched in water. In every case, the resulting microstructure was the equilibrium structure containing the phase fields β, (β + γ) and γ besides the (α + β) phase field on the left of β phase and (γ + δ) phase field on the right of the γ phase. Fig. 7 shows a representative micrograph with the β, (β + γ) and γ phase fields. No phase similar to the ζ phase of Schürmann and co-workers was observed.

From these results it is concluded that the Al - Mg phase diagram as presented in the recent assessment of Al - Mg binary systems by Murray[6] is more accurate than that proposed by Schürmann and co-workers[7,8]. However, the peritectoid temperature for the formation of R is 405 ± 5°C instead of 370 ± 5°C as indicated by Murray[6]. The existence of a lower temperature limit for the equilibrium existence of R is still not resolved but must be below 305 ± 5°C since R phase precipitated from the (β + γ) phase field at this temperature (Table I). The phase diagram for the Al - Mg system as reported by Murray[6] but with the temperature range of the R phase corrected from the results of this investigation is reproduced in Fig. 8.

Conclusion:

1. A technique for the rapid determination of binary phase diagrams has been developed and applied in studying the Al-Mg system.
2. It has been shown that the Al-Mg phase diagram as reported by Murray[6] is basically correct except that the R phase forms at 405 ± 5°C not 380°C. Also, the lower limit for the existence of the R phase extends to 305°C and may go lower but it was not possible to establish an exact lower temperature because of the sluggishness of transformations involving the R phase.
3. The R phase does not exist at temperatures above 405 ± 5°C and therefore cannot form via a peritectic reaction as indicated by Schürmann and co-workers[7,8].
4. The (β + γ) phase field is stable at temperatures between 405°C and the melting point. No evidence for the existence of the ζ (AlMg) phase reported by Schürmann and co-workers[7,8] was found.

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8. E. Schürmann and I.K. Geissler, "Phase Equilibria in the Solid condition of the Aluminum Ysp. the Magnesium Rich corner of the Ternary System of Aluminum Lithium-Magnesium: Part III. Phase Equilibria in the solid condition of the Binary System of Aluminum-Magnesium", Giessereiforschung, 32(4), 167-170 (1980) in German.

9. M. Hansen, Constitution of Binary Alloys, McGraw-Hill, New York, 2nd Ed. (1958) See P. 105-110.

Table I Summary of Results of Heat-treated Diffusion Couples With Various Heat Treatment Temperatures and Times

Composition Range of Couples	Heat Treatment Temp (°C) ± 5°C	Time (Days)	Phases Present
30 wt. % Mg-70 wt. % Mg	280	5	β, γ
	420	5	β, γ
	310	7	β, R, γ
	370	7	β, R, γ
	400	7	β, R, γ
	305	14	β, R, γ
	410	14	β, γ
	280	21	β, γ
	*280	21	β, R, γ
35 wt. % Mg-47 wt. % Mg	435	14	β, γ
&	410	14	β, γ
30 wt. % Mg-70 wt. % Mg			
	435	14	α, β, γ, δ
0 wt. % Mg - 100 wt. % Mg	410	14	α, β, γ, δ
(Al-Mg)	400	14	α, β, R, γ. δ

* This couple contained R phase which was obtained from a previous heat treatment of 7 days at 370°C

Figure Captions:

Fig. 1 Hypothetical Binary System AB.

Fig. 2a Concentration Gradient, as-cast couple.

Fig. 2b Concentration Gradient, couple heat-treated at T.

Fig. 3 Standard 9mm Diffusion couple.

Fig. 4 General Arrangement of Phase field in an as-cast Al-Mg couple.

Fig. 5 Microstructures of an as-cast Al-30 wt. % Mg and Al-70 Wt. % Mg couple: a) (α + β) region, Mag. X200, b) β - region, Mag. X50, c) (β + γ) region, Mag. X400, d) γ - region, Mag. X50, e) (γ + δ) + γ region, Mag. X400, and f) (γ + δ) region, Mag. X1000.

Fig. 6a Al-30 wt. % Mg and Al-70 wt. % Mg couple heat treated at 370 ± 5°C for 7 days and water quenched showing precipitation of the R phase. β, (β + R), (R + γ) phase fields can be seen. Mag. X50.

Fig. 6b Same couple as in Fig. 6a (same area) with an additional heat-treatment at 280°C for 21 days followed by water quenching. R phase which was formed by annealing at 370 ± 5°C does not dissolve. Mag. X50.

Fig. 7 Al-35 wt. % Mg and Al-47 wt. % Mg couple diffused at 525°C for 30 minutes, furnace cooled to 435°C, kept at 435°C for 48 hrs and then quenched in water. Only β, β + γ and γ phase fields are seen and there is no sign of ζ phase as reported by Shurmann and co-workers[7,8]. Mag. X30.

Fig. 8 Al-Mg binary phase diagram of Murray[6] with corrected temperature range of the R phase.

Fig. 1

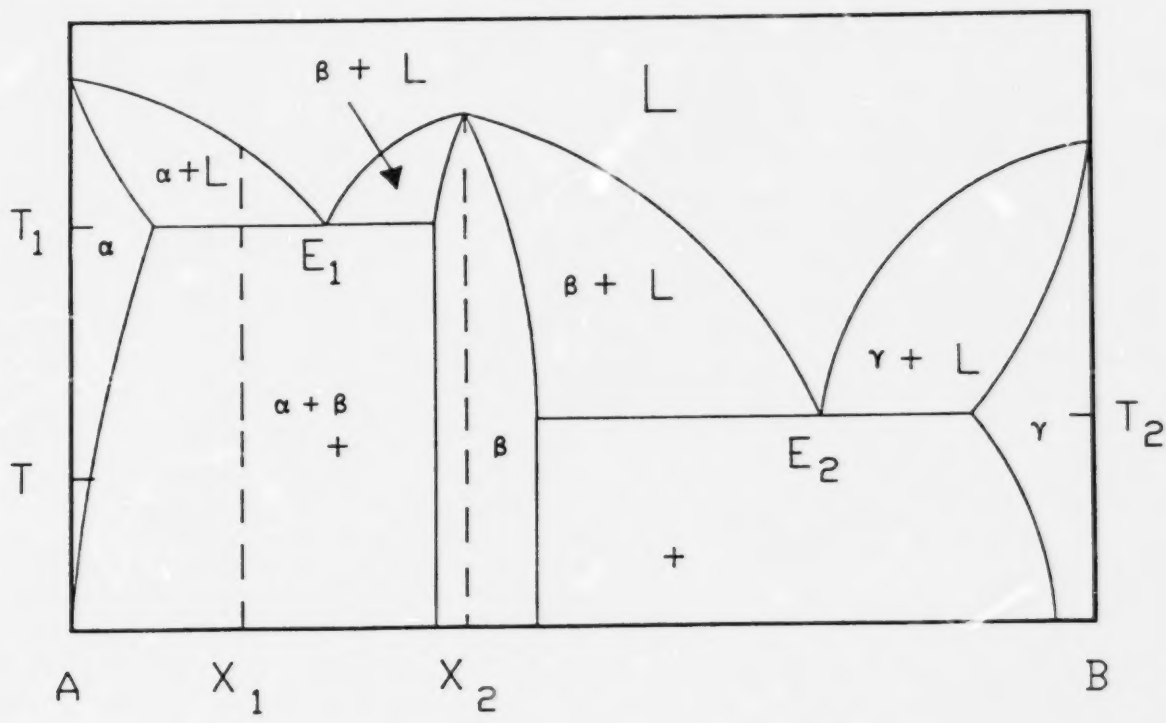


Fig. 2a.

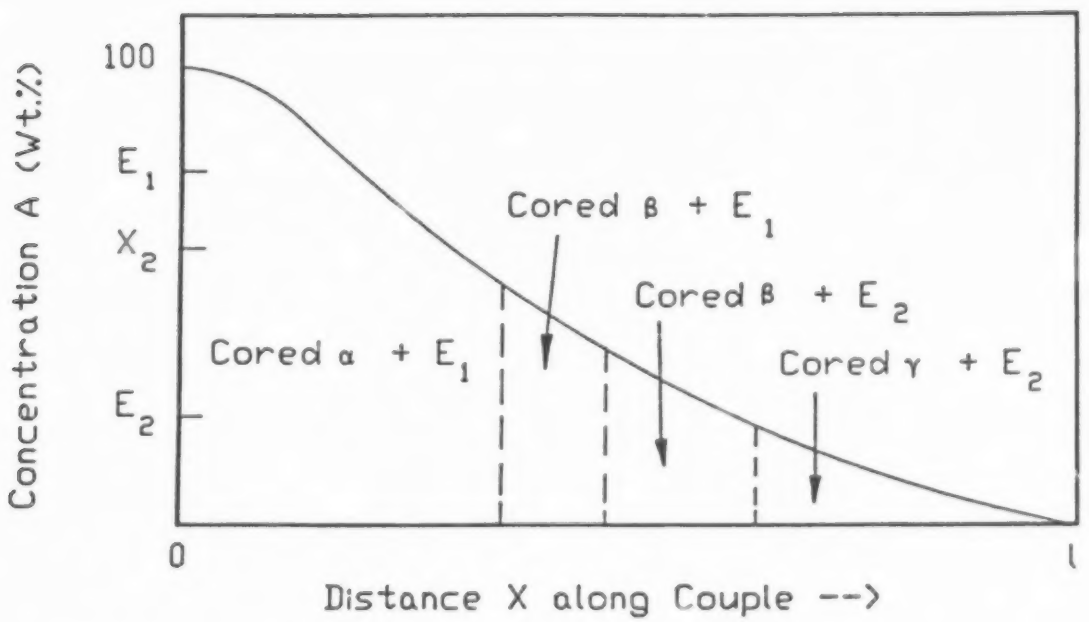

Concentration A (Wt.%)
100
E_1
X_2
E_2
Cored β + E_1
Cored β + E_2
Cored α + E_1
Cored γ + E_2
0
l
Distance X along Couple -->

Fig. 2b.

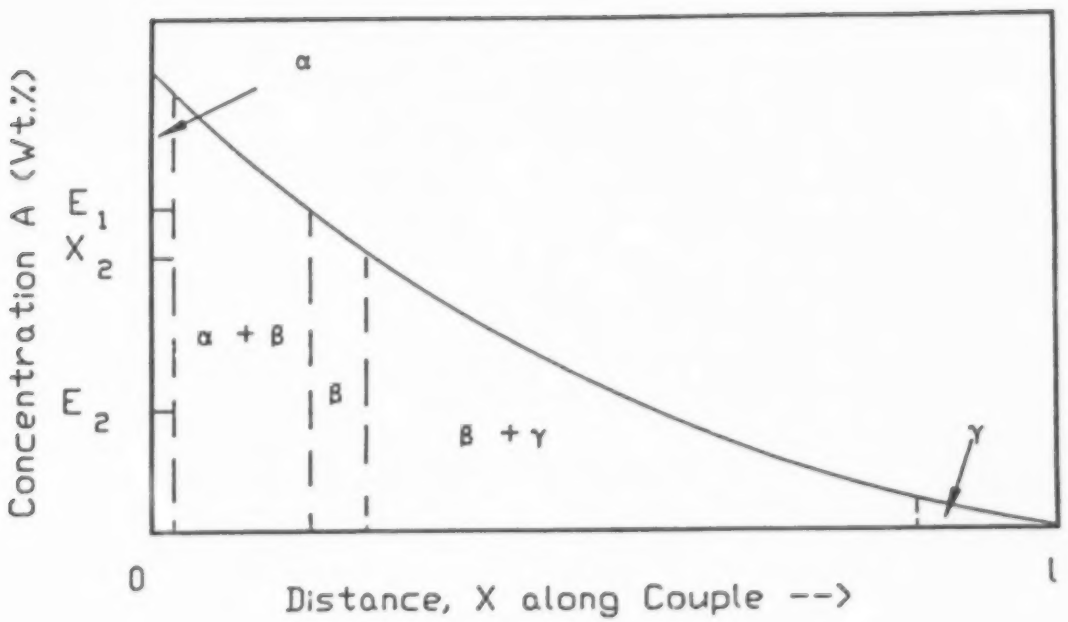
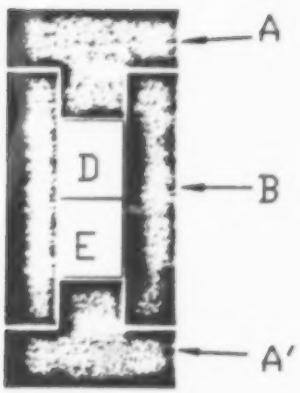

α
E 1
X 2
α + β
E 2
β
β + γ
γ
Concentration A (Wt.%)
0
l
Distance, X along Couple -->

Fig. 3

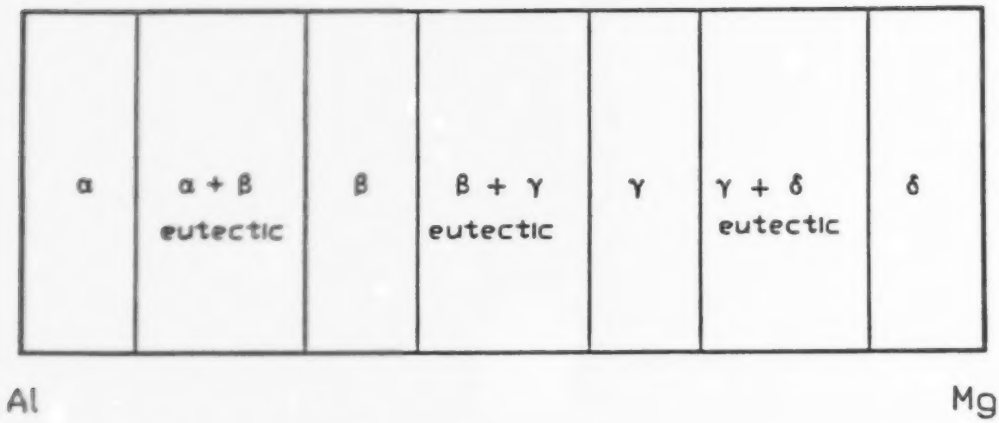


A,A' - Graphite Caps

B - Graphite Die

D,E - Two Halves of the Couple

Fig. 4



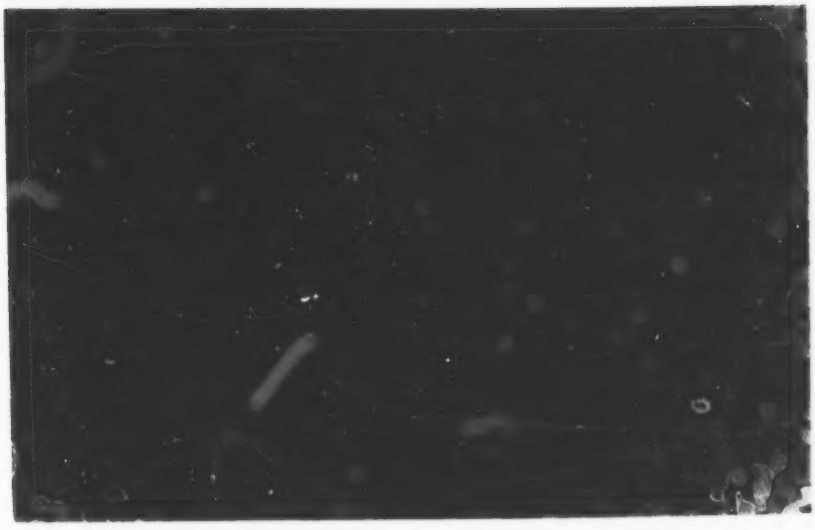


FIG. 5A

FIG. 5B

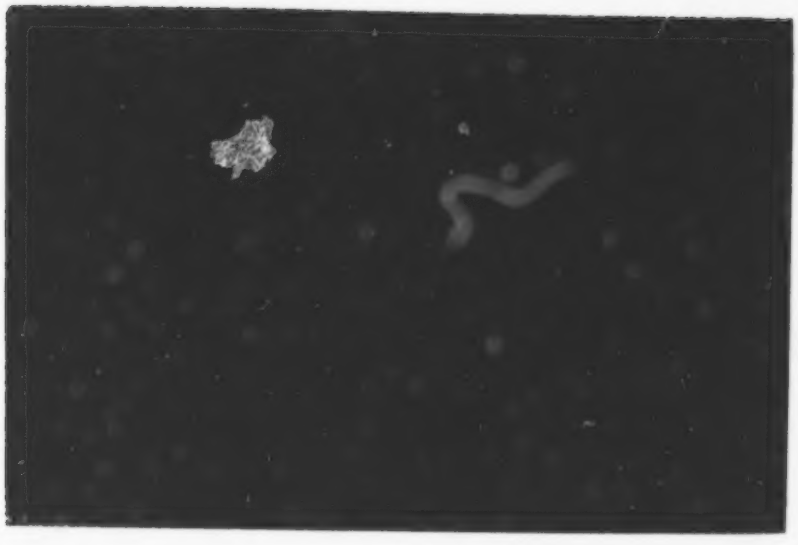


FIG. 5c

FIG. 5D

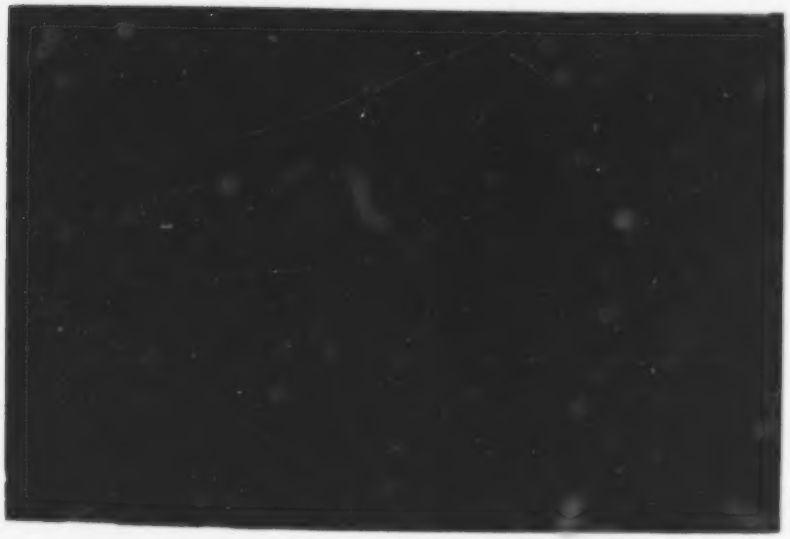


FIG. 5E

FIG. 5F

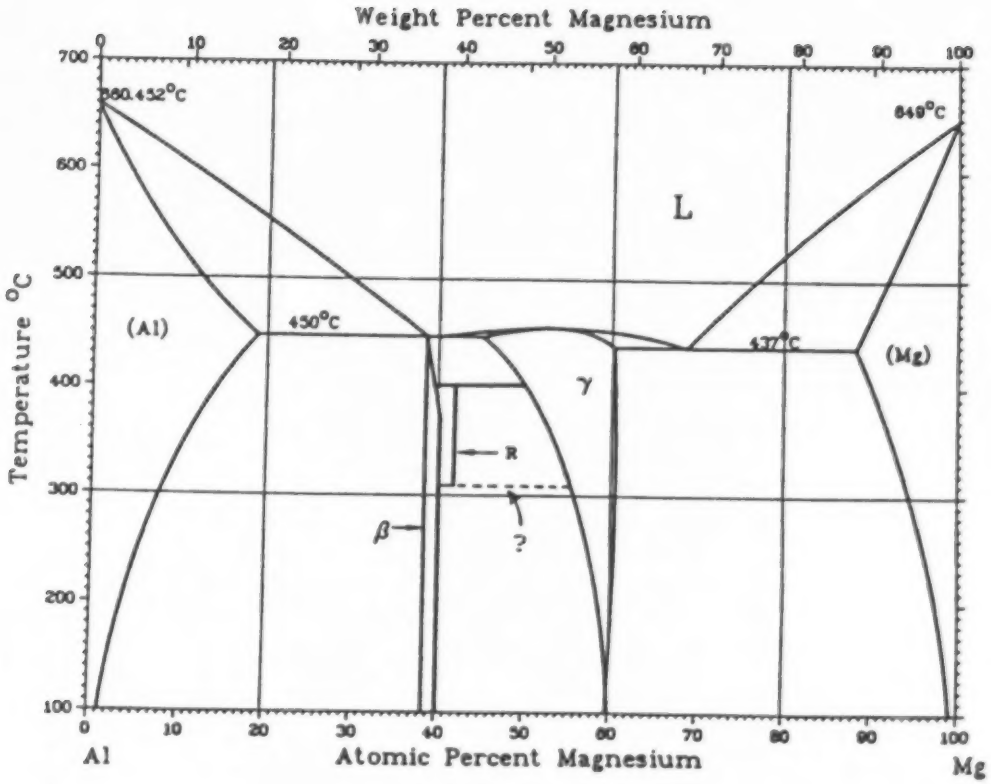
FIG. 6A

FIG. 6B

β β + γ γ

FIG. 7

FIG. 8


Weight Percent Magnesium
0
10
20
30
40
50
60
70
80
90
100
700
600
500
400
300
200
100
660.452°C
649°C
L
(Al)
450°C
437°C
(Mg)
γ
R
β
?
Temperature °C
0
10
20
30
40
50
60
70
80
90
100
Al
Atomic Percent Magnesium
Mg

APPENDIX A

Modification of the Liquidus Projection of the Al-Li-Mg System:

In Part I, 'The Al-Li-Mg (Aluminum - Lithium - Magnesium) System", of this report, we have adopted the Al-Mg binary system of [77SCH, 80SCH, 81SCH] instead of that given by [82MUR] for the evaluation of Al-Li-Mg ternary system. [81SCH] have reported the existence of the phases ζ (AlMg) and ε through a reaction scheme which is different from that given by [82MUR]. Whereas their ε phase can be identified with the R phase of [82MUR], the ζ(AlMg) phase has been uniquely reported by them only. The portion of the speculative liquidus projection between the γ ($Al_{12}Mg_{17}$) and β (Al_3Mg_2) phases (Figs. 6 and 6a, Part I) was accordingly constructed incorporating the results of [81SCH]. However, our extensive work on the study of phase relationships in the middle part (particularly between the β and γ phases) of the Al-Mg binary system, as described in Part VII of this report, suggests that other than the temperature range for the existence of the R Phase the Al-Mg Phase diagram is best represented by that of [82MUR] and not by that of [81SCH].

Therefore, the speculative liquidus projection for the Al-Li-Mg ternary system (Figs. 6 and 6a) would be modified as shown in Figs. 1 and 2 of this appendix.

In the modified liquidus projection, the three ternary peritectic reaction $P_1(u_6)$, $P_2(u_7)$ and $P_3(u_8)$ would be replaced by a single ternary eutectic reaction E_2 as follows:

$$L \underset{449°C}{\overset{\text{eutectic}}{\rightleftharpoons}} (Al) + Al_3Mg_2 + Al_{12}Mg_{17}.$$

The eutectic composition is the same as that for the reaction u_8 (P_3), i.e., Al = 58.3%, Li = 1.0%, Mg = 40.7%.

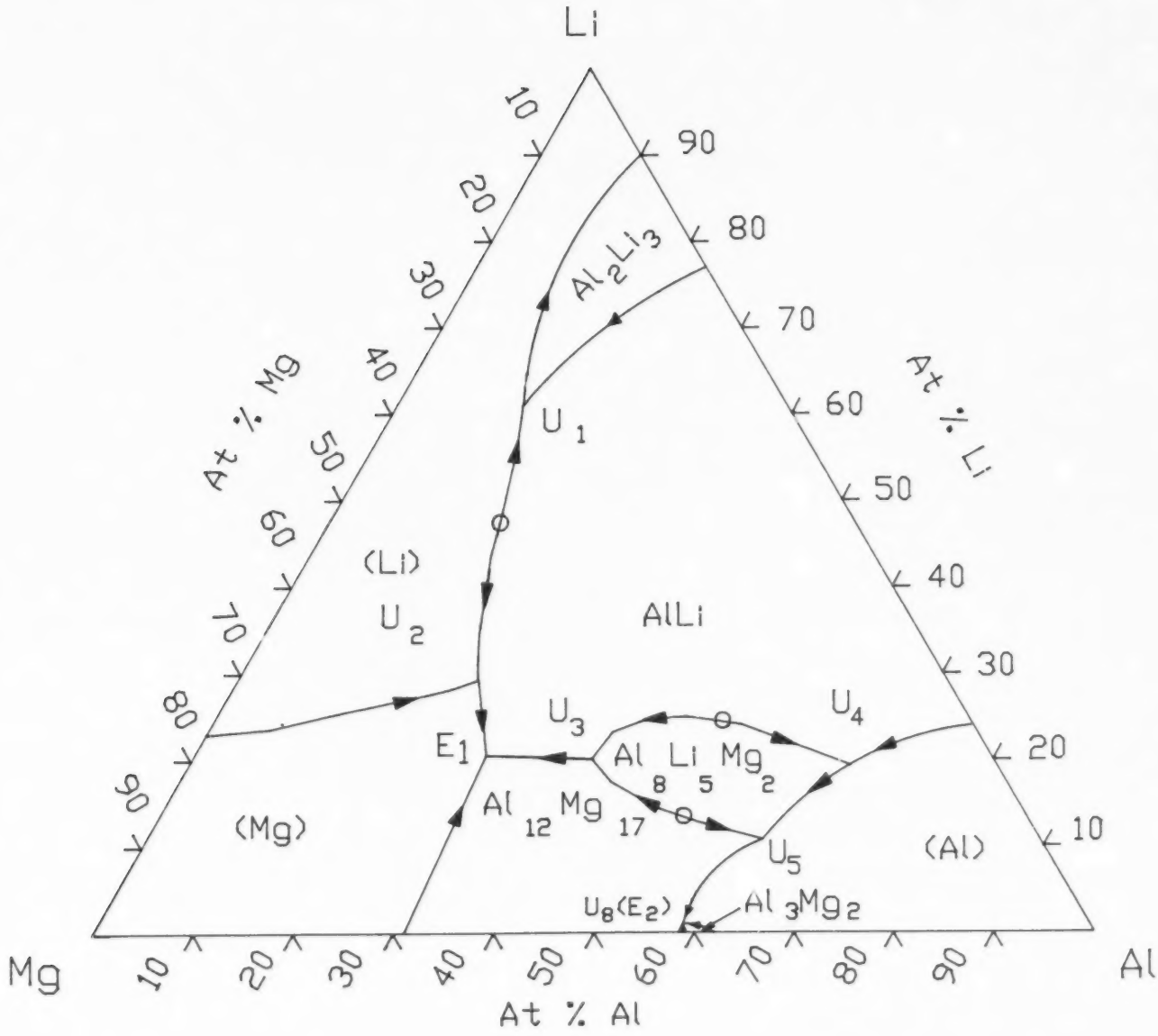


Fig. 1 Speculative Lquidus for Al-Li-Mg System
(Modification of Fig. 6, Part I)

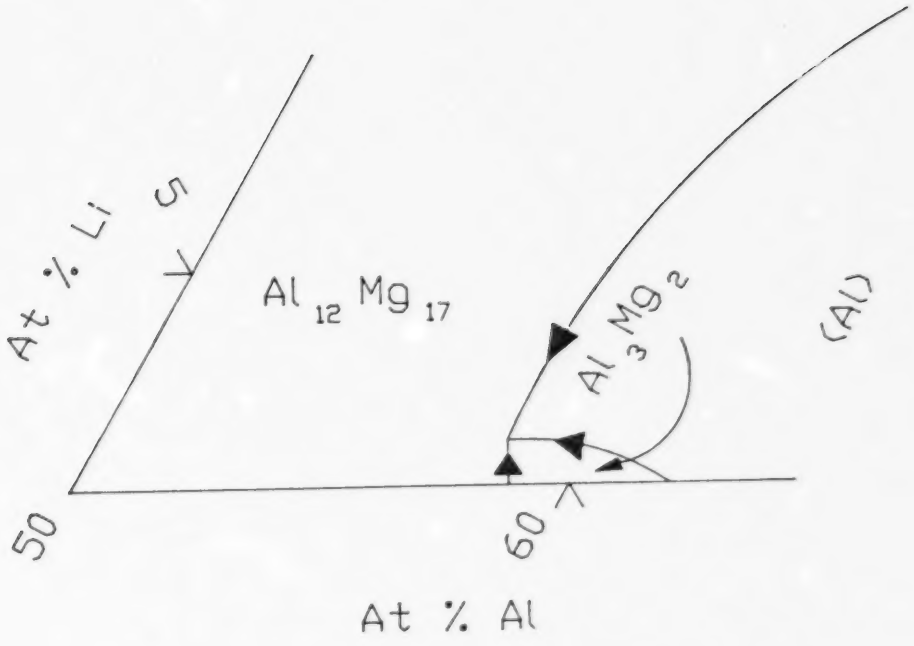


Fig. 2 Expanded Portion of the Speculative Liquidus in the Middle Part of Al-Mg Binary (Modification of Fig.6a, Part I)

APPENDIX B

Survey of More Al-Li-X (where X = Cr, Zr, Co, Mo, Ni, Be, V, Nb, Gd, Ti, Na, K and Hg) Systems:

In addition to the Al-Li-X systems reported in Part VI of the report, several other Al-Li-X systems with X = Cr, Zr, Co, Mo, Ni, W, Be, V, Nb, Gd, Ti, Na, K and Hg were exclusively searched and no relevant information pertaining to the equilibrium phase relationships in these systems was found. The search consisted of chemical abstracts, metals abstracts and world aluminum abstracts.